QUANTAL FACTORS IN THE JOULE–THOMSON COOLING OF HYDROGEN AND DEUTERIUM

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Summary

This paper presents a theoretical analysis of the Joule-Thomson cooling of normal hydrogen and deuterium from an initial temperature of 64 °K. Below 70 atm the cooling is greater for H_2 than for D_2, but at higher pressures it is less. It is found that the difference at low pressures is due to the lower heat capacity of H_2, associated with the more quantized rotation of its molecules. The difference at high pressures is due to the less negative enthalpy of imperfection of H_2, and this in turn can be attributed to the higher zero-point energy for translational motion in the lighter isotope. Both differences can be accounted for quantitatively.

I. Introduction

The deviation of a real gas from the ideal gas laws arises from two factors: (i) the existence of finite forces of attraction and repulsion between the molecules of the gas, and (ii) the failure of the approximate classical mechanical description of the gas to agree with the correct quantum mechanical description. The first factor is important at all temperatures, but the second is only appreciable at low temperatures and for light gases.

The isotopes H_2 and D_2 provide a means of separating the two effects. The similarity in behaviour of these gases at high temperatures (Michels and Goudeket 1941) shows that there is no significant difference between their intermolecular forces, and it follows that any deviations in their behaviour at low temperatures can be attributed to quantum effects. Johnston, Bezman, and Hood (1946) and Johnston, Swanson, and Wirth (1946) have observed marked deviations of this sort in the Joule-Thomson cooling of the two gases at temperatures between 64 and 80 °K. Their results at 64 °K are presented in Figure 1, which shows that at low pressures the cooling is greater for hydrogen than for deuterium, but that this order is reversed at about 70 atm. It is the purpose of the present paper to consider the reasons for these differences.

II. Some General Thermodynamic Relations

The Joule-Thomson coefficient of a gas is defined as

$$\mu=\left(\frac{\partial T}{\partial P}\right)_H, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and it is related to the equation of state by the formula

$$\mu=\left[T\left(\frac{\partial V}{\partial T}\right)_P-V\right]\Big/C_P, \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

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where T is the absolute temperature, V is the molar volume of the gas, and C_P is its molar heat capacity at constant pressure. If we write the equation of state in the virial form:

$$PV/RT = 1 + B/V + C/V^2 + D/V^3 + \ldots, \quad \ldots\ldots\ldots\ldots \quad (3)$$

then μ is given by the relation

$$\mu = \frac{1}{C_P^0}\left\{T\frac{\mathrm{d}B}{\mathrm{d}T} - B + \frac{1}{V}\left[2B^2 - 2TB\frac{\mathrm{d}B}{\mathrm{d}T} - 2C + T\frac{\mathrm{d}C}{\mathrm{d}T} + \frac{RT^2}{C_P^0}\frac{\mathrm{d}^2B}{\mathrm{d}T^2}\left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right)\right] + \ldots\right\} \quad \ldots\ldots\ldots\ldots \quad (4)$$

(cf. Hirschfelder, Curtiss, and Bird 1954). The quantities B and C are known as the second and third virial coefficients, and depend on the temperature but

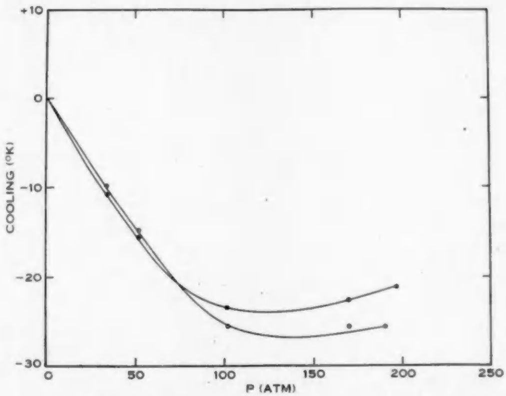

Fig. 1.—The Joule-Thomson cooling of normal hydrogen (dots) and deuterium (circles) for expansion from an initial pressure P and temperature 64 °K, to a final pressure of 1 atm.

not on the pressure of the gas. In the limit of large volumes and low pressures, equation (4) reduces to the simple form

$$\mu^0 = \frac{1}{C_P^0}\left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where the superscript 0's indicate the limiting values of the quantities at zero pressure.

Johnston, Swanson, and Wirth (1946) suggested that the trends shown in Figure 1 imply that the lower virial coefficients are numerically larger for hydrogen than for deuterium, whereas the reverse is true of the higher coefficients. Clearly this is an over-simplification, because μ depends not only on the virial coefficients but on their temperature derivatives and on C_P^0. The discussion in Section III will show that the second virial coefficient B is actually *smaller* for hydrogen than for deuterium, and that the larger value of μ^0 for hydrogen is really due to the lower heat capacity of this gas.

III. Low Pressures

(a) *Virial Coefficients*

There have been no direct measurements of the second virial coefficient of D_2 in the range of temperatures covered by the Joule-Thomson experiments, but we can make a reliable estimate of their values by using a quantal extension of the method of Lennard-Jones (1924, 1938). The basis of this calculation is the assumption that the interaction potential between two hydrogen or two deuterium molecules is effectively spherical and can be represented by the general expression

$$\varphi(r)=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where r is the distance between the centres of the interacting molecules, σ is their collision diameter, and $-\varepsilon$ is the minimum potential energy corresponding to the separation $r/\sigma=2^{1/6}$. For H_2 and D_2, these parameters have the values

$$\varepsilon=5\cdot 11\times 10^{-15}\text{ erg},$$
$$\sigma=2\cdot 93\text{ Å},$$

(cf. Hirschfelder, Curtiss, and Bird 1954).

In the absence of quantum effects the classical second virial coefficient is

$$B_{\mathrm{Cl}}=-2\pi N\int_0^\infty (\mathrm{e}^{-\varphi(r)/kT}-1)r^2\mathrm{d}r, \quad \ldots\ldots\ldots\ldots \quad (7)$$

where N is Avogadro's number, and k is Boltzmann's constant. But for hydrogen and deuterium it is necessary to apply quantum corrections for (i) the finite spacing of the translational energy levels of the molecules, and (ii) the difference between Bose-Einstein and Boltzmann statistics. The total virial coefficient then becomes :

$$B=B_{\mathrm{Cl}}+B_1+B_2+\ldots+B_{\mathrm{B\text{-}E}}, \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

where B_1 and B_2 are the first- and second-order quantum corrections arising from the factor (i), above, and $B_{\mathrm{B\text{-}E}}$ is the Bose-Einstein correction. Uhlenbeck and Beth (1936) have shown that B_1 and B_2 are given by

$$B_1=+2\pi N\Lambda^{*2}\left(\frac{\sigma^2\varepsilon}{48\pi^2k^3T^3}\right)\int_0^\infty \mathrm{e}^{-\varphi(r)/kT}\left(\frac{\mathrm{d}\varphi(r)}{\mathrm{d}r}\right)^2 r^2\mathrm{d}r, \quad \ldots\ldots \quad (9)$$

$$B_2=-2\pi N\Lambda^{*4}\left(\frac{\sigma^4\varepsilon^2}{1920\pi^4k^4T^4}\right)\int_0^\infty \mathrm{e}^{-\varphi(r)/kT}\left[\left(\frac{\mathrm{d}^2\varphi(r)}{\mathrm{d}r^2}\right)^2 +\frac{2}{r^2}\left(\frac{\mathrm{d}\varphi(r)}{\mathrm{d}r}\right)^2+\frac{10}{9rkT}\left(\frac{\mathrm{d}\varphi(r)}{\mathrm{d}r}\right)^3-\frac{5}{36k^2T^2}\left(\frac{\mathrm{d}\varphi(r)}{\mathrm{d}r}\right)^4\right]r^2\mathrm{d}r. \quad \ldots \quad (10)$$

In these formulae Λ^* is a characteristic quantal parameter defined (de Boer 1940 ; see also de Boer and Michels 1938) by

$$\Lambda^*=\frac{h}{\sigma\sqrt{(m\varepsilon)}}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

where h is Planck's constant and m is the mass of the interacting molecules. Physically Λ^*† is the de Broglie wavelength of relative motion of two molecules

† Throughout this paper asterisks are used to denote dimensionless quantities.

with relative kinetic energy ε, divided by their collision diameter σ. For H_2 and D_2 it has the values 1·73 and 1·22 respectively.

Kahn and Uhlenbeck (1938) showed that $B_{B\text{-}E}$ is given by

$$B_{B\text{-}E}=-\frac{N}{16}\Lambda^{*3}\left(\frac{\sigma^2\varepsilon}{\pi kT}\right)^{3/2}. \qquad (12)$$

To proceed with the numerical calculation of B we can use the integrated forms of (**7**), (**9**), (**10**) which de Boer (1940) derived for the particular potential (**6**). The results are given in Table 1.

TABLE 1

CALCULATED SECOND VIRIAL COEFFICIENTS OF H_2 AND D_2

The units of B are cm³ mole⁻¹

T (°K)	Hydrogen					Deuterium				
	B_{Cl}	B_1	B_2	$B_{B\text{-}E}$	B	B_{Cl}	B_1	B_2	$B_{B\text{-}E}$	B
51·8	−43·57	+18·96	−8·14	−0·53	−33·28	−43·57	+9·43	−2·01	−0·18	−36·33
59·2	−33·31	+14·49	−5·22	−0·43	−24·47	−33·31	+7·21	−1·29	−0·15	−27·54
66·6	−25·72	+11·57	−3·58	−0·36	−18·09	−25·72	+5·75	−0·88	−0·13	−20·98
74·0	−19·87	+ 9·54	−2·55	−0·31	−13·19	−19·87	+4·74	−0·63	−0·11	−15·87

By interpolation we find that at 64 °K the values of B and its temperature derivative are :

	H_2	D_2
B (cm³ mole⁻¹)	−20·15	−23·00
$\mathrm{d}B/\mathrm{d}T$ (cm³ mole⁻¹ deg⁻¹)	+ 0·830	+ 0·856
$T(\mathrm{d}B/\mathrm{d}T)-B=\mu^0C_P^0$ (cm³ mole⁻¹)	+73·30	+77·78

It will be seen that both B and $\mathrm{d}B/\mathrm{d}T$ are numerically greater for D_2 than for H_2. This is in agreement with Schäfer's (1937) experimental findings in the temperature range 20–46 °K, but in disagreement with Johnston's conclusions from the Joule-Thomson data.

(*b*) *Heat Capacities*

Woolley, Scott, and Brickwedde (1948) have made a critical survey of the values of C_P^0 for normal H_2 and D_2, and by interpolating in their tables we find that, at 64 °K, $C_P^0=207\cdot6$ cm³ atm mole⁻¹ deg⁻¹ for H_2, and 274·7 cm³ atm mole⁻¹ deg⁻¹ for D_2. The heat capacity of hydrogen is smaller than that of deuterium because its rotational degrees of freedom are less fully excited at this temperature (cf Fowler and Guggenheim 1949).

(*c*) *Joule-Thomson Coefficients*

Combining the data given in Section III(*a*) and (*b*), we find the following values of μ^0 in deg atm⁻¹ at 64 °K :

	Calc.	Expt.
H_2	0·353	0·323
D_2	0·283	0·286

The agreement between the experimental and calculated values is remarkably good for D_2, and the discrepancy for H_2 is possibly due to the neglect of the higher order quantum corrections B_3, B_4, ...

IV. High Pressures

The virial formula (4) is unsuitable for a theoretical analysis of the Joule-Thomson data at high pressures, because the necessary quantum corrections to the third and higher virial coefficients are very complex. Instead it is more profitable to consider the results on the basis of the approximate cell theory of Lennard-Jones and Devonshire (1937). The most convenient way of doing this is to use the theory to estimate the enthalpies of imperfection of the gases, $\Delta^i H = H^P - H^0$, and then compare these values with the experimental enthalpies which Johnston and co-workers (1946) derived from their Joule-Thomson measurements.

Table 2

The quantities y^* and $d \log y^*/d \log v^*$

v^*	y^*	$\frac{d \log y^*}{d \log v^*}$	v^*	y^*	$\frac{d \log y^*}{d \log v^*}$
2·31	0·175	0·950	4·31	0·280	0·594
2·45	0·185	0·906	4·71	0·295	0·566
2·60	0·195	0·872	5·16	0·310	0·538
2·84	0·210	0·800	6·03	0·335	0·484
3·31	0·235	0·720	7·02	0·360	0·449
3·83	0·260	0·648	8·25	0·385	0·402

Since we are interested primarily in the *difference* in behaviour of H_2 and D_2 it will be sufficient to consider merely the quantum corrections to the classical Lennard-Jones and Devonshire model, and the way in which these affect the enthalpy of imperfection. The Lennard-Jones and Devonshire theory assumes that each molecule in a dense fluid is effectively imprisoned in a cell bounded by its nearest neighbours. The system as a whole therefore obeys Boltzmann statistics and the only quantum correction we need apply is that for the finite spacing of the energy levels for translational motion within the cells. This correction was derived in the form of an infinite power series in Λ^* by de Boer and Lunbeck (1948), but unfortunately the series is not rapidly convergent for hydrogen at low temperatures. The author (Hamann 1952 ; David and Hamann 1953) has proposed an alternative treatment which involves some physical and mathematical simplifications but has the advantage of giving the quantum correction in a simple algebraic form. Essentially it consists in replacing the complex Lennard-Jones and Devonshire field by a " square " potential well of roughly the same shape, and then estimating the difference between the partition functions for quantized and classical motion within the well. A simple extension

of the earlier calculations shows that the quantal contribution to the enthalpy of imperfection for such a model is

$$\frac{\Delta^i H_{qu}}{RT}=\left(\frac{5}{2}+\frac{3}{2}\,\frac{\mathrm{d}\log y^*}{\mathrm{d}\log v^*}\right)\bigg/(x^*-1), \qquad \ldots\ldots\ldots\ (\mathbf{13})$$

for $x^*>1\cdot3$. In this formula,

$$x^*=9\cdot071y^{*1/2}T^{*1/2}v^{*1/3}\Lambda^{*-1},$$
$$v^*=V/N\sigma^3,$$
$$T^*=kT/\varepsilon,$$

and y^* is related to v^* by the equation

$$(1+12y^*+25\cdot2y^{*2}+12y^{*3}+y^{*4})(1+y^*)^{-1}(1-y^*)^{-6}-2v^{*2}=0. \quad \ldots\ (\mathbf{14})$$

Some values of y^* and the derivative $\mathrm{d}\log y^*/\mathrm{d}\log v^*$ are given in Table 2.

TABLE 3

QUANTAL ENTHALPIES OF IMPERFECTION OF H_2 AND D_2 AT 64 °K

$T^*=1\cdot730$

At Particular Volumes					At Particular Pressures		
v^*	Hydrogen		Deuterium		P (atm)	Hydrogen	Deuterium
	P (atm)	$\Delta^i H_{qu}/RT$	P (atm)	$\Delta^i H_{qu}/RT$		$\Delta^i H_{qu}/RT$	$\Delta^i H_{qu}/RT$
2·31	205·8	1·397	174·8	0·891	0	0	0
2·60	156·7	1·195	136·3	0·771	25	0·280	0·190
3·31	101·6	0·899	94·3	0·590	50	0·515	0·363
4·31	71·9	0·687	66·9	0·457	75	0·720	0·500
5·16	59·3	0·587	56·0	0·393	100	0·887	0·617
7·02	43·9	0·459	42·2	0·310	125	1·040	0·723
8·25	37·7	0·406	36·6	0·275	150	1·167	0·819
∞	0	0	0	0	175	1·274	0·896
					200	1·380	0·964

Since Λ^* is greater for H_2 than for D_2 it follows from equation (**13**) that $\Delta^i H$ will be more positive for the lighter isotope. Basically, this difference arises from the fact that the zero-point energy for translational motion varies inversely as the molecular mass and becomes an important part of the total energy when the molecules are confined in small spaces at high pressures.

Formula (**13**) gives $\Delta^i H_{qu}$ as a function of the reduced volume v^*, but for the purpose of comparison with Johnston's experimental results we need to know it as a function of the pressure. This conversion can readily be made from plots of the isotherms of D_2 and H_2 at 64 °K, based on (i) the second virial coefficients at low pressures, (ii) Johnston and White's (1950) *P-V-T* data for H_2 at moderate pressures, (iii) David and Hamann's (1953) *P-V-T* data for H_2 and D_2 at high pressures. The results of the calculations are listed in Table 3,

and the difference $(\Delta^i H_{qu})_{H_2}-(\Delta^i H_{qu})_{D_2}$ has been plotted against pressure in Figure 2.

It will be seen that there is good agreement between the theoretical curve and the experimental differences in the enthalpies of imperfection of the two gases.

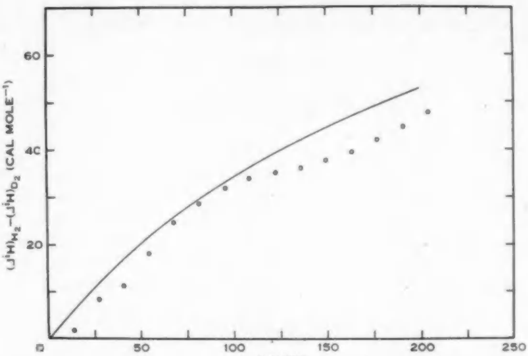

Fig. 2.—The difference between the enthalpies of imperfection of normal hydrogen and deuterium at 64 °K.

○ From Johnston's experimental values; the curve represents the theoretical difference $(\Delta^i H_{qu})_{H_2}-(\Delta^i H_{qu})_{D_2}$ taken from Table 3.

V. Conclusions

The conclusions to be drawn from this analysis are:

(i) The low-pressure Joule-Thomson cooling is greater for hydrogen than for deuterium because hydrogen has the lower heat capacity of the two isotopes. This difference, in turn, arises from the less classical rotation of its molecules.

(ii) At high pressures the difference in heat capacities is outweighed by the fact that hydrogen has a less negative enthalpy of imperfection than deuterium. This latter difference arises from the greater zero-point energy and the wider spacing of the energy levels for translational motion in the lighter isotope.

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NUCLEOPHILIC SUBSTITUTION REACTIONS AT HIGH PRESSURE

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Summary

The rates of a number of nucleophilic substitution reactions have been measured over a range of pressures to 3000 atm. Reactions where ions are produced in the rate-determining step are accelerated 4·0–4·6 times, while where there is no change in the number of ions, the acceleration is by a factor of 2·25. In the solvolysis of *iso*propyl bromide, which proceeds by simultaneous S_N1, S_N2, and $E2$ mechanisms, of differing electrical type, it is shown that high pressures favour the S_N1 mechanism.

I. Introduction

Hamann and his collaborators (Buchanan and Hamann 1953; David and Hamann 1954; Hamann and Teplitzky 1956) have shown that the effect of pressure on liquid-phase ionic reactions is closely related to their electrical nature. An increase in the number of charges at the rate-determining step produces a large increase in the rate at high pressures, and conversely, a decrease in the number of charges retards the rate; while if there is no net change in the number of charges, there is usually a small increase in the rate. In the present paper, the rates of solvolyses of a series of alkyl bromides have been investigated. The results, in accordance with the above rules, show that for a simple reaction where ions are produced, the rate is more than quadrupled at 3000 atm, while if there is no change in the number of ions, the rate at 3000 atm is only about twice that at atmospheric pressure.

The series that has been investigated comprises: (i) The neutral solvolysis of methyl bromide; (ii) the neutral solvolysis of ethyl bromide; (iii) the alkaline solvolysis of methyl bromide; (iv) the neutral solvolysis of *iso*propyl bromide; and (v) the solvolysis of *iso*propyl bromide in alkaline solution. The reaction mechanisms involved (Ingold 1953) are shown in Table 1.

The mechanisms applicable in reactions (i) to (iv), which are kinetically pure, are given in Table 2, column 2. In the alkaline solvolysis of *iso*propyl bromide, however, the S_N1, $S_N2(b)$, and $E2$ mechanisms occur simultaneously (Hughes, Ingold, and Shapiro 1936). Since there is a net increase in charge only in the S_N1 mechanism, the proportion of the solvolysis proceeding by the S_N1 mechanism is expected to be increased with higher pressures. The present measurements demonstrate this quantitatively.

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TABLE 1

REACTION MECHANISMS*

R denotes an alkyl group, R′ an alkyl group or hydrogen atom, and X a halogen atom

Reaction	Mechanism	Change in No. of Charges at Rate-Determining Step	Expected Change in Reaction Rate with Increases in Pressure
S_N1 solvolysis	$RX \rightarrow R^+ + X^-$ (slow) $R^+ + R'^- \rightarrow ROR'$ (fast)	+2	Large increase
S_N2 (type *a*) solvolysis ..	$RX + R'OH \rightarrow ROR' + X^- + H^+$	+2	Large increase
S_N2 (type *b*) solvolysis ..	$RX + R'O^- \rightarrow ROR' + X^-$	0	Small increase
$E2$ elimination solvolysis ..	$CH_3.CHX.CH_2R + R'O^-$ $\rightarrow CH_2:CH.CH_2R + R'OH + X^-$	0	Small increase

* Ingold (1953).

II. EXPERIMENTAL

B.D.H. methyl, ethyl, and *iso*propyl bromides and absolute ethanol were dried and subsequently distilled, the constant boiling point middle fractions being retained. The alkyl bromides were added by weight to the dry ethanol. Volumetric additions of water or aqueous alkali started the reactions. Reactions (i), (ii), and (iii) were carried out in a solvent which at atmospheric pressure consisted of 80 parts by volume of ethanol to 20 parts by volume of water, while the solvent for reactions (iv) and (v) was 60 parts by volume of ethanol to 40 of water. In the alkaline solvolyses the initial and final concentrations were determined by titrating with 0·02N hydrochloric acid, while in the neutral solvolyses the final acid concentrations were found by titrating with 0·02N barium hydroxide. Bromothymol blue was used as indicator. In the solvolyses of *iso*propyl bromide approximately 0·105N concentrations of both *iso*propyl bromide and, where required, sodium hydroxide were used. The high pressure equipment and the techniques employed have been described by Buchanan and Hamann (1953) and by Weale (1954). Temperatures during the experiments were controlled to within 0·1 °C, and the high pressures were maintained to within 50 atm.

III. RESULTS AND DISCUSSION

All the reactions were measured over different times, and their rate constants calculated from the usual formulae. The first-order rate constants $\mathbf{k}_1$ (in sec^{-1}) for reactions (i), (ii), and (iv); and the second-order rate constant $\mathbf{k}_2$ ($sec^{-1}\ mol^{-1}\ l$) for reaction (iii) did not vary significantly with time (at the 1 per cent. significance level). Their mean values at atmospheric pressure, $\mathbf{k}_{(1)}$, and the ratios, $\mathbf{k}_{(p)}/\mathbf{k}_{(1)}$, where $\mathbf{k}_{(p)}$ indicates the rate constant at p atm pressure, are listed in Table 2. The values of $\mathbf{k}_{(1)}$ are of the magnitude expected from earlier measurements (Hughes, Ingold, and Shapiro 1936 ; Bateman *et al.* 1940). The

values of the ratios $\mathbf{k}_{(p)}/\mathbf{k}_{(1)}$ agree with similar work recently reviewed elsewhere (Strauss 1957). For the reactions (i), (ii), (iii), which were carried out in the same solvent, the ratios $\mathbf{k}_{(p)}/\mathbf{k}_{(1)}$ are plotted in Figure 1.

TABLE 2

RATES OF SOLVOLYSES REACTIONS AT HIGH PRESSURE

Reaction	Type	Solvent	Temperature (°C)	Rate at Atmospheric Pressure, $\mathbf{k}_{(1)}$ (sec^{-1})	$\mathbf{k}_{(p)}/\mathbf{k}_{(1)}$		
					$p=1000$	$p=2000$	$p=3000$
(i) CH_3Br + solvent	S_N2 (*a*)	80% ethanol	45	$\mathbf{k}_1 \cdot 10^6 = 1 \cdot 2$	1·68	2·51	4·00
(ii) C_2H_5Br + solvent	S_N2 (*a*)	80% ethanol	50	$\mathbf{k}_1 \cdot 10^6 = 1 \cdot 0$	1·72	2·80	4·07
(iii) CH_3Br + OH^-, $OC_2H_5^-$*	S_N2 (*b*)	80% ethanol	0	$\mathbf{k}_2 \cdot 10^5 = 5 \cdot 7$ (mol^{-1} l)	1·40	1·75	2·25
(iv) $(CH_3)_2CHBr$	S_N1	60% ethanol	45	$\mathbf{k}_1 \cdot 10^6 = 2 \cdot 22$†	—	—	4·60

* Previously published by David and Hamann (1954).
† Value from Hughes, Ingold, and Shapiro (1936).

If, in the solvolysis of *iso*propyl bromide in alkaline solution, the initial concentrations of the reactants (*iso*propyl bromide and sodium hydroxide) are

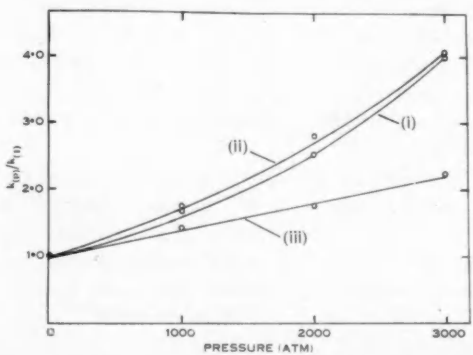

Fig. 1.—The effect of pressure on simple nucleophilic substitution reactions in 80 per cent. ethanol solution. The numbers on the curves indicate the reaction (Table 2).

made equal, the three mechanisms S_N1, $S_N2(b)$, and $E2$, will all occur simultaneously to a measurable extent. The proportion of product obtained through the first-order S_N1 mechanism can be isolated from the second-order $S_N2(b)+E2$

mechanism by the method outlined by Hughes, Ingold, and Shapiro (1936). When the usual equation for a first-order reaction $k_1 t = \ln a/(a-x)$, where a is the initial concentration of *iso*propyl bromide, and x is the quantity used after time t, is applied to the present experimental data for the combined mechanisms, a series of values of k_1, which decrease with time, are obtained. Lines to fit these were calculated by the method of least squares. These are :

At 1 atm $\qquad k_1 \times 10^5 = 0 \cdot 686_6 - 1 \cdot 11_6 \times 10^6 \ (t-84300)$;

At 3000 atm $\qquad k_1 \times 10^5 = 2 \cdot 62_6 - 1 \cdot 40_7 \times 10^5 \ (t-18300)$.

The line at atmospheric pressure agrees closely with that found experimentally by Hughes, Ingold, and Shapiro. From the rate constant for reaction (iv), $\mathbf{k}_1$ and the equations of these lines, the independent second-order rate constant for the $S_N2(b)+E2$ reaction can be calculated from an equation deduced from one by these workers (Ingold 1953)

$$\mathbf{k}_2 = (k_1 + t.\mathrm{d}k_1/\mathrm{d}t - \mathbf{k}_1)/(a-x).$$

The quantity of the reactant used by the first order, S_N1, solvolysis, x_1, can then be found from

$$x_1 = -\mathbf{k}_1/\mathbf{k}_2 \ln\left[1 - x/(\mathbf{k}_1/\mathbf{k}_2 + a)\right].$$

The quantity x_1 was calculated for a series of values of x ($x = 0 \cdot 01, 0 \cdot 02, \ldots, 0 \cdot 05$ mol l^{-1}) covering the range of experimental determinations. At atmospheric pressure, the ratio of x_1 to x was found to be almost constant at 29·5 per cent. At 3000 atm, x_1/x has an average value of 38·9 per cent., 9·4 per cent. greater. At high pressure the ratio increased slightly from 37·7 per cent. at $x = 0 \cdot 01$ mol l^{-1} to 40·8 per cent. at $x = 0 \cdot 05$ mol l^{-1}. This increase can be explained by the probable non-linear relation of k_1 with time. The linear relation had to be assumed, as an accuracy greater than that obtainable with present techniques used at high pressures would be required to determine a non-linear relation.

The increase of almost 10 per cent. in the proportion of the S_N1 reaction is highly significant, as uncertainties in the technique and the scatter of experimental results show that the errors at 3000 atm are probably only of the order of 2 per cent. Higher pressures will give far greater effects, but these could be eclipsed by the larger experimental errors, which can possibly be as high as 30 per cent. at 15000 atm (David and Hamann 1954).

IV. Acknowledgments

The author wishes to express his appreciation of the facilities and assistance provided by Dr. K. E. Weale, Department of Chemical Engineering, Imperial College of Science and Technology, where the *iso*propyl bromide rate studies were carried out ; and also to Dr. S. D. Hamann of the C.S.I.R.O. High Pressure Laboratory, University of Sydney, for his help with the earlier work.

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MAGNETIC SUSCEPTIBILITY OF TRI-COORDINATED COPPER(II) COMPLEXES*

By M. Kishita,† Y. Muto,‡ and M. Kubo†

[*Manuscript received May 20, 1957*]

Summary

The magnetic susceptibilities of salicylal-*o*-hydroxybenzylamine Cu(II), salicylal-*o*-hydroxyanil Cu(II), acetylacetone-mono-(*o*-hydroxyanil) Cu(II), and benzoylacetone-mono-(*o*-hydroxyanil) Cu(II), as well as their pyridinates, have been measured by the Gouy method at room temperature. The effective magnetic moments calculated from the data of the pyridine-free complexes per one copper atom are smaller than the theoretical moment, 1·73 B.M., for one odd electron. Although it has been presumed from the method of synthesis, the chemical analysis of the complexes, and the tridentate nature of the ligand molecules that the copper atoms of the chelates have the unusual coordination number 3, the subnormal magnetic moments suggest the presence of dimeric molecules, in which two copper atoms are very close to each other as in cupric acetate monohydrate. On the other hand, the pyridinates have normal magnetic moments expected for tetra-coordinated copper complexes.

I. Introduction

It has been believed for the following reason that the magnetic criterion does not give much information on the structure of cupric complexes. A cupric ion has one unpaired electron with a magnetic moment close to 1·73 Bohr magnetons (B.M.). A covalent copper atom also has one odd electron regardless of the configuration of ligands attached to it: the square bond type resulting from dsp^2 hybridization and the tetrahedral coordination of ligands by use of sp^3 orbitals lead to the presence of one odd electron in the $4p$ and $3d$ orbital of the central metal atom, respectively (Martell and Calvin 1952). Rây and Sen (1948) showed that the magnetic moments of cupric complexes fall into two groups: those in one group show a moment ranging in 1·72–1·82 B.M. while those in the other group have a greater moment of 1·90–2·20 B.M. They interpreted the results in terms of the more or less complete quenching of orbital moment of the single unpaired electron raised to the outermost $4p$ level in the case of planar dsp^2 coordination and accordingly exposed to the influence of the electrons of neighbouring atoms. They believed that it was possible to distinguish between dsp^2 covalent complexes and ionic or sp^3 covalent complexes by this

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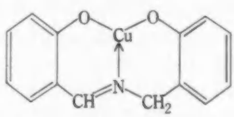
criterion. Although a number of magnetochemical studies have been made on copper(II) complexes, almost all of them consider copper of coordination number 4. In order to test the interpretation of magnetic moments, it seems worth while to extend magnetic measurements to a wide variety of complex compounds involving divalent copper.

So-called tri-coordinated copper complexes have been reported by several investigators. For instance, Pfeiffer *et al.* (1937) have prepared salicylal-*o*-aminophenol Cu(II), while Yamaguchi (1953) and Muto (1953, 1955) have synthesized salicylal-*o*-hydroxybenzylamine (or salicylal-salicylamine) Cu(II). From the method of synthesis, the chemical analysis of the complexes, and the tridentate nature of the ligand molecules, it is presumed that the copper atoms of these chelates have the unusual coordination number 3, although no direct evidence for this coordination number has been afforded as yet by physical methods such as X-ray crystal analysis. One of the present authors (Y.M.) has prepared a number of similar copper chelates and their pyridinates. This paper presents the results of magnetochemical study on these complexes.

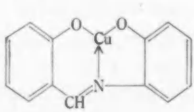
II. Preparation of Materials

(*a*) *Salicylal-o-hydroxybenzylamine Cu(II).*—Salicylaldehyde was subjected to condensation



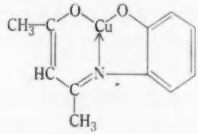
with *o*-hydroxybenzylamine in an ethanol solution. The resulting Schiff's base was separated and was treated with cupric acetate in the mixture of ethanol and water. The crude product, which precipitated, was separated, dissolved in pyridine, and filtered. When water was added to the filtrate, the pyridinate of this copper chelate was obtained. On heating at an appropriate temperature (80–90 °C), almost all the pyridine was removed. To ensure the complete removal, the residue was boiled in ethanol on a water-bath for about half an hour. After being allowed to cool, the precipitate was filtered, and dried at about 90 °C. In this way, a pyridine-free copper complex was obtained. The chelate was readily soluble in pyridine, slightly soluble in nitrobenzene, and soluble with difficulty in other common organic solvents. Therefore, recrystallization was repeated in the form of the pyridinate in order to purify this sample. Both the chelate and its monopyridinate are green prismatic crystals (Found: Cu, 22·0; N, 5·0%. Calc. for $C_{14}H_{11}O_2NCu$: Cu, 22·0; N, 4·9%. Found: Cu, 17·3; N, 7·6%. Calc. for $C_{14}H_{11}O_2NCu.C_5H_5N$: Cu, 17·3; N, 7·6%).

(*b*) *Salicylal-o-hydroxyanil Cu(II) or Salicylal-o-aminophenol Cu(II).*—This compound and



those listed below were prepared by essentially the same method as that described above using different starting materials. The copper chelate is green, while its monopyridinate is brown. Both crystallize in prisms (Found: Cu, 23·36; N, 5·0%. Calc. for $C_{13}H_9O_2NCu$: Cu, 23·1; N, 5·1%. Found: Cu, 18·0; N, 7·8%. Calc. for $C_{13}H_9O_2NCu.C_5H_5N$: Cu, 18·0; N, 7·9%).

(c) *Acetylacetone-mono-(o-hydroxyanil) Cu(II).*—This compound forms deep green prismatic



crystals. The monopyridino-compound crystallizes as deep green plates (Found: Cu, 25·4; N, 5·4%. Calc. for $C_{11}H_{11}O_2NCu$: Cu, 25·1; N, 5·5%. Found: Cu, 19·2; N, 8·4%. Calc. for $C_{11}H_{11}O_2NCu.C_5H_5N$: Cu, 19·2; N, 8·4%).

(d) *Benzoylacetone-mono-(o-hydroxyanil) Cu(II).*—This chelate has a constitutional formula identical with that of the foregoing copper complex, except a phenyl group is substituted for a methyl group on the left-hand side. It forms yellow-green needles. The corresponding pyridinate crystallizes as deep green plates (Found: Cu, 20·1; N, 4·6%. Calc. for $C_{16}H_{13}O_2NCu$: Cu, 20·2; N, 4·5%. Found: Cu, 16·1; N, 7·3%. Calc. for $C_{16}H_{13}O_2NCu.C_5H_5N$: Cu, 16·1; N, 7·1%).

None of these pyridine-free complexes melted below 300 °C. The pyridinates liberated pyridine gradually at 70 °C and completely at 120 °C. The decrease in weight corresponded to one molecule of pyridine per one atom of copper. In order to prevent partial decomposition, the pyridinates were kept in desiccators placed in a refrigerator.

III. Apparatus and Experimental Results

For the determination of magnetic susceptibility, a Gouy magnetic balance (Kondo *et al.* 1956) was employed at room temperature (14 °C). The sample tube made of hard glass was 15 cm long with a central partition making two compartments. One of them was filled with the powder crystals under investigation, while the other was empty. The internal diameter of the tube was 3 mm. The cell was suspended between the poles of an electromagnet from a semi-micro-balance capable of determining weight changes as small as 0·01 mg. The electromagnet could be supplied with a direct current of up to 17 A taken from selenium rectifiers, ripples having been removed by means of a series of condensers. The rectifiers were fed from a 200-V, three-phase A.C. source, which was stabilized with an appropriate voltage stabilizer, and was led through suitable transformers before it was applied to the rectifiers. The total resistance of the coil of the electromagnet was less than 3 Ω. Each tip of the pole pieces, which were separated from each other by about 1 cm, had a circular surface plane of 3 cm in diameter. The resulting magnetic field could be raised to about 24,000 oersteds, although no such strong field was required in the present experiment. The magnetic balance was calibrated with distilled water, its magnetic susceptibility per gram being set equal to $-0 \cdot 720 \times 10^{-6}$.*

From the apparent susceptibility per unit volume $\varkappa'$, and the apparent density d', of a crystal mass packed as uniformly as possible, the magnetic susceptibility χ per gram of a copper chelate was calculated with due regard to the paramagnetism of air:

$$\chi=\frac{\varkappa'}{d'}-\frac{\varkappa_{\mathrm{air}}}{d'}+\frac{\varkappa_{\mathrm{air}}}{d},$$

* Throughout the present paper, the data of magnetic susceptibility are given in c.g.s., e.m.u.

where $\varkappa_{air}$ denotes the volume susceptibility of air. The true density d of crystals appeared only in a correction term. Accordingly, its accuracy was of minor importance for the observed values of magnetic susceptibility of crystals. The results are presented in Table 1.

Allowing for the diamagnetic contributions of the chelated groups and assuming the validity of Curie-Langevin's law, the effective magnetic moments μ per one atom of copper in the chelates were calculated as shown in the last column of Table 1. In this case, the diamagnetic contributions of ligands were

TABLE 1

THE MAGNETIC SUSCEPTIBILITIES (PER GRAM) AND THE MAGNETIC MOMENTS OF TRI-COORDINATED COPPER COMPLEXES AND THEIR PYRIDINATES

Chelates	χ (c.g.s., e.m.u.)	μ (B.M.)
Salicylal-*o*-hydroxybenzylamine Cu(II) ..	$0{\cdot}705\times10^{-6}$	0·87
Monopyridino-salicylal-*o*-hydroxybenzylamine Cu(II)	3·48	1·83
Salicylal-*o*-hydroxyanil Cu(II)	2·41	1·34
Monopyridino - salicylal - *o* - hydroxyanil Cu(II)	3·70	1·84
Acetylacetone - mono - (*o* - hydroxyanil) Cu(II)	2·81	1·37
Monopyridino - acetylacetone - mono - (*o* - hydroxanil) Cu(II)	3·85	1·81
Benzoylacetone - mono - (*o* - hydroxyanil) Cu(II)	1·25	1·11
Monopyridino - benzoylacetone - mono - (*o*-hydroxyanil) Cu(II)	3·25	1·84

calculated from Pascal's constants. They were subject to certain ambiguity as to the constitutive correction constants. In order to test the accuracy of the calculated values, the molar susceptibility of salicylal-*o*-hydroxybenzylamine was measured and the contribution from two hydrogen atoms was subtracted from it. The value was 126, while the calculated one was also 126. The perfect agreement may be fortuitous, but suggests that for other chelates showing greater moments than that of salicylal-*o*-hydroxybenzylamine Cu(II), the error inherent in the estimation of the diamagnetic contributions will cause no appreciable change in the calculated moment, that is, an error less than 1 per cent. in the moment.

The only magnetic data found in literature on this type of compounds are those for salicylal-*o*-hydroxyanil Cu(II) reported by Calvin and Barkelew (1946), who gave 1040×10^{-6} for its molar paramagnetic susceptibility at 25 °C. This corresponds to 1·57 B.M., a value slightly greater than that of the present investigation.

IV. Discussion

The moments of pyridinates falling in the range 1·81–1·84 B.M., as shown in Table 1, are normal values expected for cupric complexes. If the fact is taken into account that the pyridinates readily lose pyridine, the observed moments represent the lower limit, the true values being presumed to be somewhat greater. The excess of these values over the theoretical moment of 1·73 B.M. for one odd electron is attributable to the orbital contribution. According to the theory of Rây and Sen (1948), this fairly great excess suggests the tetrahedral coordination. These authors have found that planar dsp^2 covalent complexes are black, brown, red, or greenish yellow, while the colour of ionic or tetrahedral sp^3 covalent complexes is green, blue, or blue-violet. All the pyridinates studied in the present investigation have a deep green colour, except monopyridino-acetylacetone-mono-(*o*-hydroxyanil) Cu(II), which is brown. Although it is difficult to make a definite choice between the tetrahedral and the square coordination from the observed magnetic moments of the copper complexes, the fairly great orbital contribution, the colour of the chelates, and the structure of tridentate ligand molecules make the square coordination less likely, compared with the tetrahedral arrangement of ligands.

On the other hand, the moments of pyridine-free complexes are abnormally small. In fact, they are smaller than the theoretical value predicted from the presence of one unpaired electron. Calvin and Barkelew (1946) also obtained a subnormal moment of 1·57 B.M. for salicylal-*o*-hydroxyanil Cu(II), but they attributed the lower value to impurities. On the other hand, the present authors have found that in the course of purification by repeated recrystallization, the observed moment decreases tending to a constant value, which is smaller than that given by Calvin and Barkelew.

As has already been pointed out, a divalent copper atom has one odd electron regardless of the configuration of ligands attached to it. The hybridization of whatever type leads to the presence of an odd electron, irrespective of whether the arrangement of bonds is trigonal plane, asymmetrical plane, or trigonal pyramid (Eyring, Walter, and Kimball 1948). The method of molecular orbitals also will predict a moment greater than 1·73 B.M. The reason for this lies in the fact that the chemical formulae as given in Section II contain an odd number of atoms having an odd atomic number.

One might suspect that these chelates contain copper in the cuprous state with no unpaired electrons. However, this possibility is excluded by consideration of the method of their preparation as well as their purification.

A possible explanation for these low moments is afforded by the formation of binuclear complexes. The method of preparation and the results of chemical analysis, on which the present molecular formulae are based, do not exclude the possibility of dimer formation, leading to the presence of some kind of electron pairing taking place between two copper atoms in a molecule. This will at once recall the binuclear copper derivative of diphenylmethylarsine, $Cu_2Cl_3(Ph_2MeAs)_3$, studied by Mellor and Craig (1941 ; see also Selwood 1943). It is reported that both a blue and a brown modification have the same moment of 1·78 B.M. per molecule. If the formation of a binuclear complex is disregarded, the moment

for one copper atom would be calculated as $1 \cdot 78/\sqrt{2} = 1 \cdot 26$ B.M. and would simulate an abnormally small moment. Selwood (1956) also records that cupric acetate shows a subnormal moment due to exchange effects between adjacent copper ions, and that a substantial number of other organic derivatives of Cu(II) show somewhat similar effects. The X-ray analysis on cupric acetate monohydrate (Niekerk and Schoening 1953) has revealed that the real unit composing the crystal is a dimeric molecule, $Cu_2(CH_3CO_2)_4(H_2O)_2$, in which the Cu–Cu distance, 2·64 A, is nearly equal to that in metallic copper, 2·551 A. The decreasing susceptibility of copper acetate found by Guha (1951) and by Figgis and Martin (1956) as the temperature is lowered, and the decreasing intensity of the paramagnetic resonance absorption observed by Bleaney and Bowers (1952) can be correlated with the close distance of approach of the two Cu atoms. In this connection, mention should be made of the recent work by Miyashita (personal communication), Hokkaido University, on the paramagnetic resonance absorptions of three of the samples used in the present investigation. He could observe no absorption of salicylal-*o*-hydroxybenzylamine Cu(II), salicylal-*o*-hydroxyanil Cu(II), and acetylacetone-mono-(*o*-hydroxyanil) Cu(II) at room temperature. However, the corresponding monopyridino-compounds showed an absorption at a *g*-value equal to about 2·2. Details will be published elsewhere.

To conclude, it seems very likely that the so-called tri-coordinated copper complexes have structures not so simple as implied by their ordinary chemical formulae. The magnetic data suggest the presence of dimeric molecules, in which two copper atoms are very close to each other. In pyridinate formation, presumably the Cu–Cu links are broken, yielding tetra-coordinated complexes having normal magnetic moments.

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AN ELECTROKINETIC STUDY BY THE STREAMING POTENTIAL METHOD OF ION EXCHANGE AT OXIDE MINERAL SURFACES

By P. G. JOHANSEN* and A. S. BUCHANAN*

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Summary

The streaming potential method has been used to observe changes in the electrical double layer at the surfaces of the minerals Al_2O_3, SnO_2, Fe_2O_3, and TiO_2 in the presence of electrolytes. In addition to the normal effects of preferential physical adsorption of ions, ion exchange involving surface hydroxyl groups offers a useful hypothesis for explaining the results. Anion-exchange mechanisms appeared to be of particular importance in the reactions of phosphate, molybdate, and citrate with the oxide surfaces. In general for the particular samples used, Al_2O_3 and SnO_2 (having basic surfaces) exhibited more pronounced anion exchange than Fe_2O_3 and TiO_2 which had acidic surface.

I. INTRODUCTION

In several earlier papers on this subject it has been shown that the hydrated surfaces of insoluble oxides such as SnO_2 (O'Connor and Buchanan 1953), Al_2O_3 (O'Connor, Johansen, and Buchanan 1956), and SiO_2 (O'Connor and Buchanan 1956) are capable of displaying ion-exchange phenomena. Hydroxyl groups on the hydrated surface of the mineral may behave either as acids or bases in aqueous medium, depending upon the extent to which they are polarized by neighbouring metal atoms in the crystal lattice.

For alumina it was found that the material not ignited generally behaves as a base, the surface ionizing and exchanging hydroxyl ions readily. However, ignition to 1000 °C causes the surface to become acidic, protons now being released more readily than complete hydroxyl ions. This change is presumably due to an increase in the polarization of surface hydroxyl groups. Silica, on the other hand, was always found to exhibit an acid surface, the sign of the surface charge being negative.

The present paper records an extension of the observations on the surface properties of Al_2O_3 and SnO_2 and lists also the results of parallel studies on Fe_2O_3 and TiO_2. The exchange of anions such as phosphate and molybdate received particular attention since it seemed that the method might be of some value in elucidating the problems of retention and subsequent release of these ions by the mineral constituents of soils (cf. Jones and Milne 1956).

II. EXPERIMENTAL

The streaming potential method was used and the experimental details were identical in all respects with those previously described (O'Connor, Johansen, and Buchanan 1956). In this preceding paper the results were expressed as surface

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charge densities, calculated from ζ-potentials. Allowance is made in this way for variation of diffuse layer thickness with change in electrolyte concentration. For present purposes, however, the lengthy recalculations are not necessary since we are chiefly concerned with comparing the effects of the same electrolytes in the same concentration ranges on a number of different oxides. Moreover, with electrolytes such as ammonium molybdate the ionic constitution is uncertain due to polymerization and condensation, and hence the calculation of surface charge densities becomes uncertain. We are therefore expressing results as ζ-potential-concentration curves, the ζ-potential being calculated from the measured streaming potential (E) using the Helmholtz-Smoluchowski equation, namely,

$$\zeta = -\frac{4\pi\eta\varkappa.E}{D.P},$$

where D is the dielectric constant (taken to be that of water in all cases), η the viscosity of the liquid (water at the experimental temperature), P the pressure forcing liquid through the plug, and $\varkappa$ the conductivity of liquid contained in the pores of the plug.

In the subsequent discussion we assume that the ζ-potential-concentration curves give an approximate measure of the variations in surface charge density produced by ion-exchange and adsorption processes occurring at the surfaces of the solids in contact with electrolyte solutions.

All of the solids used were massive natural crystalline materials and, before packing in the streaming cell, were ground in an iron mortar, the size range 100–500 μ selected by sieving, washed with dilute HCl, then conductivity water, and finally dried at 120 °C in an electric oven. The ferric oxide was a pure sample of specular haematite (>99·9 per cent. Fe_2O_3), the SnO_2 was a sample of cassiterite originating from South Woodburn, N.S.W., the Al_2O_3 was a sample of α-alumina containing 0·94 per cent. silica impurity, and the TiO_2 was a pure sample of rutile.

The conductivity water used in the experiments was twice distilled, the second time from slightly acidified permanganate, in an all Pyrex still. Analytical reagent chemicals were used in preparing solutions.

III. Results

The ζ-potentials of the solids in water and the variation of these potentials with the addition of acid, alkali, sodium citrate, ammonium molybdate, potassium dihydrogen phosphate and, in the case of ferric oxide, ferric ammonium sulphate, and potassium chloride also, are shown in Figures 1 to 4.

KH_2PO_4 was chosen to study the effect of phosphate retention by mineral surfaces since the ion $H_2PO_4^-$ is likely to be the most important species involved in the chemistry of acid soils. With the molybdate, phosphate, and citrate solutions, there is evidence of anion exchange occurring at the solid surfaces, the phenomena usually consisting of a slow attainment of the equilibrium value of the ζ-potential in the particular electrolyte solution.

The exchange process may usually be observed more readily in desorption when pure water is streamed through the plug of material and the ζ-potential slowly returns to its original value as hydroxyl ions replace the anions on the surface. Figure 5 shows this process occurring on the surface of α-alumina, for several different anions.

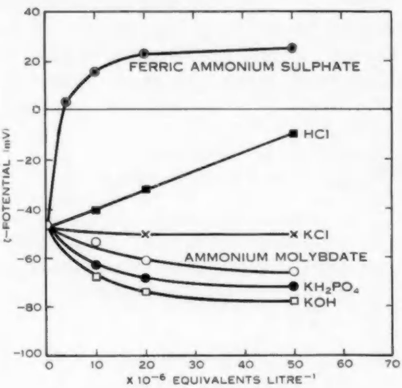

Fig. 1

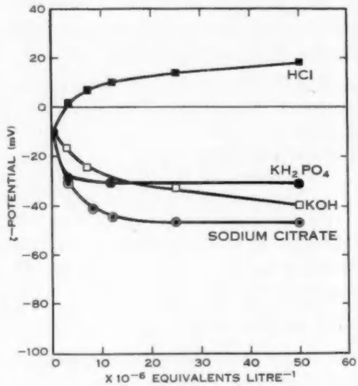

Fig. 2

Fig. 1.—Effects of electrolytes on the ζ-potential of natural Fe_2O_3, not ignited.

Fig. 2.—Effects of electrolytes on the ζ-potential of natural TiO_2 (rutile), not ignited.

IV. Discussion

The haematite sample in water has a negative (i.e. acidic) surface (Fig. 1). As noted in Section I, this implies relatively strong polarization of surface hydroxyl groups facilitating release of protons to form the diffuse layer of charge. Addition of HCl to the system will result in repression of the acid dissociation of the surface as well as forming an ionized surface chloride according to the mechanism discussed for alumina (O'Connor, Johansen, and Buchanan 1956). Both processes will tend to reduce the negative magnitude of the surface charge, which is in agreement with the experimental observations. The increase in negative potential on the addition of KOH is probably due to both cation exchange (with stronger ionization of the potassium salt as compared with the original surface acid) and preferential physical adsorption of hydroxyl ions by the haematite surface. It has been shown previously (Buchanan and Heymann 1948) that ions can be physically adsorbed by a surface already possessing a charge of the same sign, the extent of adsorption being independent of reasonable changes in the magnitude of the charge on the surface. The increases in negative potential in phosphate and molybdate will have analogous explanations, that is, anion exchange and preferential physical adsorption of anions by the surface. By comparison, KCl has very little effect and presumably gives negligible preferential ion adsorption, and in neutral solution, little ion exchange.

Ferric ammonium sulphate produces a marked reversal of charge of Fe_2O_3 in very low concentration (Fig. 1), and furthermore the charge could not be

returned to its original sign on prolonged washing with water. It seems likely that the surface of the haematite becomes coated with a layer of hydrated ferric oxide (arising from hydrolysis of the ferric ammonium sulphate) and that surface

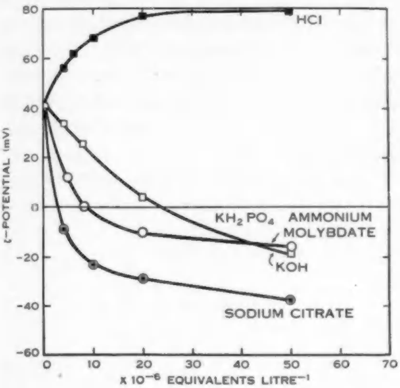

Fig. 3

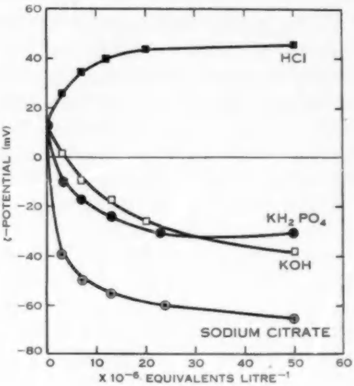

Fig. 4

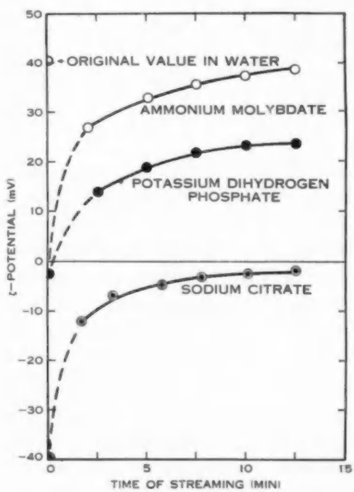

Fig. 5

Fig. 3.—Effects of electrolytes on the ζ-potential of natural α-Al_2O_3, not ignited.

Fig. 4.—Effects of electrolytes on the ζ-potential of a sample of cassiterite (natural SnO_2), not ignited.

Fig. 5.—Rate of removal of exchanged anions from the surface of α-Al_2O_3 by washing with conductivity water. The origin of each curve represents the ζ-potential reached in a concentration of 1×10^{-5} equiv l^{-1} for KH_2PO_4 and ammonium molybdate and 5×10^{-5} equiv l^{-1} for sodium citrate.

ionization of hydroxyl groups of this material confers the positive charge. Electrophoretic measurements (discussed by Johansen and Buchanan 1957) confirm that freshly precipitated ferric hydroxide has a positive (i.e. basic) surface, with an isoelectric pH considerably above 7.

The surface of the sample of rutile, as with haematite, has a negative charge although small in magnitude; it is therefore slightly acidic (Fig. 2). The behaviour towards electrolytes resembles that of haematite and similar mechanisms appear to operate. The positive surface charge produced in HCl is likely to represent the formation by anion exchange of a partly ionized surface chloride. The large increase in negative charge in citrate solution is probably due to both anion exchange and physical adsorption of multivalent citrate ions.

TABLE 1

COMPARISON OF THE BEHAVIOUR OF THE FOUR OXIDES

Solid	Initial ζ-Potential (mV)	Change in ζ-Potential Produced by Addition of 1×10^{-5} equiv l^{-1} (mV)		
		KH_2PO_4	Ammonium Molybdate	Sodium Citrate
Al_2O_3	+40	42	42	63
SnO_2	+13	34	—	65
Fe_2O_3 ..	—46	18	8	—
TiO_2	—10	20	—	32

Al_2O_3 and SnO_2 both have positive (i.e. basic) surfaces in water (Figs. 3 and 4). The increase in positive potential in HCl in each case is probably due to the formation of a partly ionized chloride on the surface, whilst the increase in negative potential on the addition of KOH follows upon cation exchange and the preferential physical adsorption of hydroxyl ions by the surface. Phosphate, molybdate, and citrate all show evidence of anion exchange and physical adsorption of anions, negative surface charges resulting in all cases. Citrate has a somewhat greater effect than molybdate or phosphate on the two solids.

A comparison of the behaviour of the four solids in anion exchange and adsorption processes (represented by the change in ζ-potential produced by equivalent concentration of added electrolyte) seem to show that alumina is the most efficient, followed closely by cassiterite, then, with a considerable gap, rutile and haematite showing effects of approximately the same magnitude (Table 1).

The initially basic surfaces, as might be expected, show the greatest powers of exchanging (and adsorbing) anions. This conclusion is in agreement with that of van Schuylenborgh (1951), who showed that an approximate relation existed between the isoelectric pH and the phosphate adsorption of a number of samples of hydrated iron and aluminium oxides; in general, the more basic substances bound phosphate most readily.

Relative rates of hydrolysis of the three anions citrate, molybdate, and phosphate, previously exchanged with hydroxyls on the alumina surface, were observed by measuring the changes in ζ-potentials as pure water was streamed through the porous plug (Fig. 5). The initial very rapid change in the direction of the original value (before exchange) is no doubt principally due to removal of physically adsorbed ions and easily hydrolysed species. The slow change thereafter probably represents the removal of more firmly bound anions. Removal of molybdate is substantially complete after about 12 min, phosphate has recovered somewhat over half the change in ζ-potential in this time, whilst citrate, which reached a large negative potential on treatment with the electrolyte, had failed to revert even to the original positive surface. The result with citrate indicates quite strong retention of some physically adsorbed citrate ions, a fact which may be associated with the ability of citrate to complex cations in aqueous solution.

Prolonged washing over some hours was found ineffective in restoring the original potential with citrate and phosphate. However, increasing the concentration of hydroxyl ions drastically (with 10^{-2}N NaOH) proved effective in bringing about complete reversal of the anion exchange.

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AN APPLICATION OF THE MICROELECTROPHORESIS METHOD TO THE STUDY OF THE SURFACE PROPERTIES OF INSOLUBLE OXIDES

By P. G. Johansen* and A. S. Buchanan*

[*Manuscript received June 12, 1957*]

Summary

The variation with pH of the electrophoretic mobility of suspended particles has been determined for Fe_2O_3, TiO_2, SnO_2, SiO_2, Al_2O_3, and for a number of synthetic aluminosilicates. The properties of the natural substances have been compared with those of synthetic materials before and after ignition at high temperatures. In general, the dehydration and recrystallization caused by ignition of the precipitated materials tend to produce surfaces resembling those of the natural crystals.

I. Introduction

In order that our studies of the surface properties of insoluble oxides might be extended to include synthetic as well as natural materials, we adapted the microelectrophoresis apparatus of Street and Buchanan (1956) to the investigation of finely-divided precipitated oxides, which, of course, cannot be conveniently investigated in the streaming potential apparatus (Johansen and Buchanan 1957), requiring relatively coarse crystalline particles.

Our objective was to compare the surface properties of freshly-precipitated washed hydrous oxides with the same materials after ignition, and then to effect a comparison with the properties of the natural materials. It is to be expected on the basis of our previous studies that the degree of polarization exhibited by surface hydroxyl groups, which determines the sign and magnitude of surface ionization, and hence the properties of the electrical double layer in water, should be considerably influenced by the previous history of the specimen.

In addition to the study of pure oxides (Fe_2O_3, TiO_2, SnO_2, SiO_2, and Al_2O_3), we also investigated a number of precipitated aluminosilicates of different compositions, the properties of which demonstrated the transition from an essentially basic surface (α-Al_2O_3) to an essentially acidic surface (SiO_2).

II. Experimental

The microelectrophoresis apparatus and technique recently described by Street and Buchanan (1956) was used without further modification. The motion of at least 10 different particles in each direction was observed for each system. The maximum deviation from the mean value for the time of traverse rarely exceeded 5 per cent., thus indicating reasonable uniformity of particle properties in each sample. Experimental temperatures were all within the range 18–20 °C, but no precise temperature control was attempted or deemed necessary.

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Street and Buchanan have calculated precise values of ζ-potentials from electrophoretic mobilities, using correction terms for surface conductivity and relaxation (the effect arising from deformation of the double layer). Since our present purpose called for the investigation of relatively large differences in the surface properties of otherwise closely related substances, it was considered sufficient to present the results simply as comparisons of mobilities which may be taken as approximately proportional to ζ-potentials. The mobilities are expressed as μ sec^{-1} per volt cm^{-1} ($1\mu=10^{-4}$ cm).

The pH of solutions was adjusted by adding appropriate volumes of HCl or NaOH solutions to very dilute suspensions of the oxides. Solutions in the electrophoresis cell were protected by glass stoppers to limit absorption of carbon dioxide during an experiment. A Cambridge glass electrode pH meter was used in the measurement of pH.

The electrophoresis samples were prepared by the following methods.

(i) *SnO_2*.—Pure tin was treated with hot dilute HNO_3 at 80 °C for 8 hr. The precipitated hydrous oxide was then filtered and washed thoroughly with conductivity water.

(ii) *TiO_2*.—The heavy oily liquid $TiCl_4$ was added to boiling water, the consequent hydrolysis yielding hydrated rutile. Ammonia was added to assist in flocculation of the precipitate, which was then filtered and washed.

(iii) *Fe_2O_3*.—Hydrous ferric oxide was produced by the addition of ammonia to ferric ammonium sulphate solution. The precipitate was washed with 5 per cent. ammonium nitrate solution and finally with conductivity water.

It may be noted that there is no evidence for the existence of definite hydroxides of tin, titanium, or iron. With the former two, the hydrous oxides obtained by precipitation have the X-ray patterns of cassiterite (SnO_2) and rutile (TiO_2), respectively (Weiser and Milligan 1939). The precipitates should therefore be regarded as oxides hydrated with indefinite amounts of water.

(iv) *Aluminosilicates*.—Sodium metasilicate was dissolved in hot distilled water, the solution acidified with HNO_3, an appropriate amount of $Al(NO_3)_3$ added, and then 0·880 sp. gr. ammonia solution until no further precipitation occurred. The white gelatinous precipitate was filtered by suction, washed with conductivity water, suspended in ammonium nitrate solution at 60 °C for 30 min (to effect exchange with ammonium ion), filtered again, and washed with water till the filtrate conductivity was less than 2×10^{-6} ohm^{-1} cm^{-1}. The aluminosilicates were analysed by volatilization of the silica on treatment with HF and H_2SO_4.

Certain of the above samples were investigated in the hydrous state as prepared, whilst others were first ignited; the ignition was carried out at 1000 °C (850 °C for SnO_2 and Fe_2O_3) in air for 2 hr. If sintering had occurred, the samples were very lightly crushed to produce particles of size suitable for the electrophoretic measurements.

The natural materials were finely ground in an iron mortar, washed with dilute HCl and conductivity water, and dried at 120 °C.

III. Results

The experimental observations are presented as curves showing the variation of particle mobility with variation of pH ; the analogous observations in streaming potential measurements are those which show the variation of ζ-potential with the addition of HCl or NaOH to the streaming solution (Johansen and Buchanan 1957).

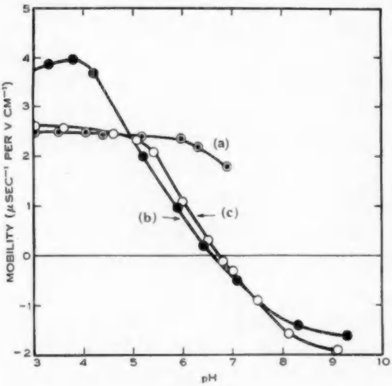

Fig. 1

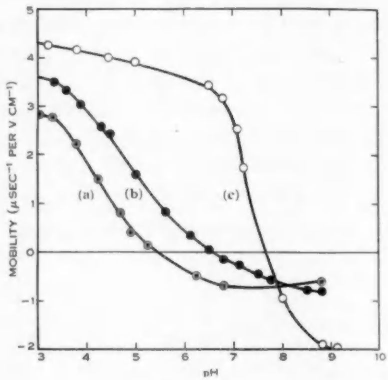

Fig. 2

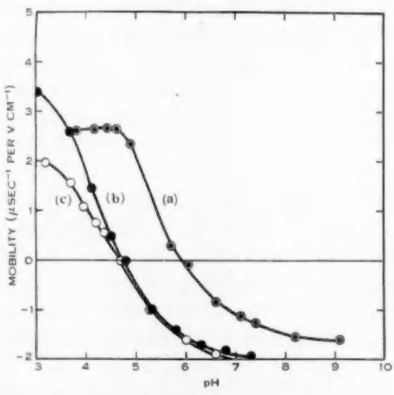

Fig. 3

Fig. 1.—Variation with pH of the electrophoretic mobility of Fe_2O_3 particles : (*a*) freshly precipitated, hydrated ferric oxide (deflocculation of the particles prevents observations above pH 7) ; (*b*) precipitated and then ignited at 850 °C for 2 hr ; and (*c*) natural ferric oxide, a pure sample.

Fig. 2.—Variation with pH of electrophoretic mobility of three samples of SnO_2 : (*a*) freshly precipitated, hydrated SnO_2 ; (*b*) precipitated and ignited at 1000 °C for 2 hr ; (*c*) natural SnO_2 from South Woodburn, N.S.W., not ignited.

Fig. 3.—Variation with pH of electrophoretic mobility of three samples of TiO_2 : (*a*) freshly precipitated, hydrated TiO_2 ; (*b*) precipitated and ignited at 1000 °C for 2 hr ; (*c*) natural TiO_2, not ignited.

Figures 1, 2, and 3 refer respectively to ferric oxide, stannic oxide, and titanium dioxide in various states, whilst Figure 4 refers to alumina, silica, and the aluminosilicates.

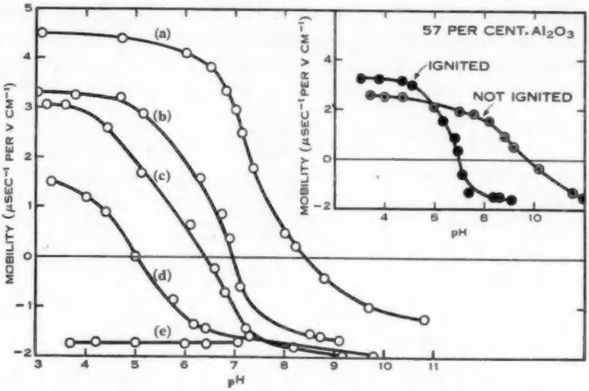

Fig. 4.—Variation with pH of electrophoretic mobility of Al_2O_3, SiO_2, and synthetic aluminosilicates: (*a*) natural α-Al_2O_3; (*b*) 57 per cent. Al_2O_3; (*c*) 48 per cent. Al_2O_3; (*d*) 34 per cent. Al_2O_3; (*e*) SiO_2; all after ignition at 1000 °C.

Inset: The change in properties of a synthetic aluminosilicate produced by ignition.

IV. Discussion

The general similarity of the velocity-pH curves in most cases is quite marked and it seems probable that there exists a common explanation, with the factors varying only in degree, from one example to another. Our streaming potential studies on the oxide systems (Johansen and Buchanan 1957) are best explained in terms of anion- and cation-exchange processes involving the added acid and alkali and hydroxyl groups on the hydrated surfaces of the oxides. There may be in addition some physical adsorption of hydroxyl ions by the surfaces in the case of added NaOH, but its contribution to the changes in mobility is usually not easy to determine. In general, the exchange processes may be represented by the following idealized equations, the broken line referring to the plane of shear, which marks the division of the diffuse layer of ions from the surface

$$>\text{M–OH}+\text{H}^+\text{Cl}^- \rightleftharpoons\ >\text{M}^+ \mid \text{Cl}^-+\text{H}_2\text{O},$$
$$>\text{M–OH}+\text{Na}^+\text{OH}^- \rightleftharpoons\ >\text{MO}^- \mid \text{Na}^++\text{H}_2\text{O}.$$

The salts formed will in general be ionized to a greater extent than the parent hydroxyl groups and hence in acid the tendency will be towards an increase in positive surface charge, the diffuse layer consisting of chloride ions, whilst in alkali the reverse tendency towards a greater negative charge will determine the nature of the electrophoretic mobility.

With the exception of pure silica, all the simple and mixed oxides to which the figures refer show positive surface charges in acid and negative charges in alkaline solution, the chief differences occurring in the pH of the isoelectric point at which the net surface charge is zero (Table 1). The value of the isoelectric pH is evidently related to the acidity of the surface hydroxyl groups, this in turn depending on the extent to which these groups are polarized by underlying metal atoms of the crystal lattice.

TABLE 1

THE ISOELECTRIC pH'S OF INSOLUBLE OXIDES

Oxide	Precipitated, Hydrated	Precipitated, Ignited	Natural, Not Ignited
Fe_2O_3 ..	8·0	6·5	6·7
TiO_2 ..	6·0	4·7	4·8
SnO_2 ..	4·5	5·5	7·3

Ignition of the hydrated material in each case changes the isoelectric pH, the change tending to make the surface approximate more closely to the natural crystals in properties. With Fe_2O_3 and TiO_2, ignition produces a more acid surface (stronger polarization of surface hydroxyl groups), whilst with SnO_2 the surface becomes less acid, implying reduced polarization of the hydroxyl groups of the surface.

Identical isoelectric pH's of synthetic/ignited and natural materials do not of course mean that the surfaces are the same in all respects. The non-coincidence of the appropriate mobility curves at low pH's in Figures 1 and 3 shows that the exchange capacities of the surfaces still differ. Furthermore, coincidence or otherwise in properties will depend on the particular sample of natural material chosen, two different samples rarely having identical surface behaviour, and quite frequently these properties may be changed by ignition (O'Connor, Johansen, and Buchanan 1956).

Ignition of one of the synthetic aluminosilicates (57 per cent. Al_2O_3) reduced the basicity of the surface hydroxyl groups markedly, the isoelectric pH changing from 9·8 to 7·0 (Fig. 4, Inset). In this respect, we have found previously (O'Connor, Johansen, and Buchanan 1956) that ignition of natural α-Al_2O_3 changes an originally positive or basic to a negative or acidic surface, possibly because re-hydration of the strongly ignited surface is limited and the surface hydroxyl groups are now subjected to stronger polarization, and hence show acidic character. Furthermore, it has been shown by X-ray diffraction studies that ignition at 1000 °C of synthetic aluminosilicates containing more than 50 per cent. Al_2O_3 results in the formation of α-Al_2O_3 (Milliken, Mills, and Oblad 1950).

The synthetic aluminosilicates show a progressive decrease in basic character as the percentage of Al_2O_3 diminishes: the isoelectric pH's are: α-Al_2O_3 8·4, 57 per cent. Al_2O_3 7·0, 48 per cent. Al_2O_3 6·4, 34 per cent. Al_2O_3 5·0 (Fig. 4).

This result is to be expected since silica itself shows no isoelectric point, the surface displaying acid behaviour down at least to pH 3. Accompanying the decrease in basic character there is also a progressive decrease in the magnitude of the positive mobility (i.e. positive surface charge) attained in the lower pH ranges. This is to be expected from the reduction in the number of basic hydroxyl groups on the surface as the percentage of Al_2O_3 diminishes. There seems to be some evidence for a corresponding increase in the negative charge attained in the higher pH range, but the results here are less clearly defined (Fig. 4).

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A NEW COMPLEX CYANIDE OF MOLYBDENUM

By M. C. Steele*

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Summary

A new cyano complex of molybdenum, potassium pentacyano molybdate(IV), $KMo(CN)_5$, has been prepared in three ways: (i) by direct reaction of molybdenum trioxide and potassium cyanide, (ii) by the oxidation of the black heptacyanide, $K_4Mo(CN)_7.2H_2O$, and (iii) by heating the brown potassium tetracyano dioxo molybdate(IV), $K_4MoO_2(CN)_4$.

I. Introduction

Cyano complexes of molybdenum have been reported with the molybdenum in the valency state of (III), (IV), and (V). The black heptacyanide with molybdenum(III) has been formulated as $K_4Mo(CN)_7.2H_2O$ (Young 1932); with molybdenum(IV), are the thoroughly investigated octacyanide $K_4Mo(CN)_8$ (Rosenheim, Garfunkel, and Kohn 1909; Bucknall and Wardlaw 1927; Jakób and Turkiewiez 1931; Young 1932; Willard and Thielke 1935; Hoard and Nordsieck 1939), the hydrated red cyanide reported by Heide and Hofmann (1896) to be $4KCN.MoO_2.10H_2O$ which is probably similar to Bucknall and Wardlaw's (1927) preparation as $K_4Mo(OH)_4(CN)_4$, and a green hydrated compound $K_3Mo(OH)_3(CN)_4.3H_2O$ (Bucknall and Wardlaw 1927). The cyanide complex of molybdenum(V) is $K_3Mo(CN)_8$ (Bucknall and Wardlaw 1927; Rawlinson 1941).

A white cyano complex $KMo(CN)_5$ is now added to this list.

The valency state of (IV) is the stable condition with molybdenum cyanides as both the black heptacyanide of molybdenum(III) and the $K_3Mo(CN)_8$ with molybdenum(V) are unstable and revert to cyanides of molybdenum(IV).

II. Discussion

The molybdenum in the white pentacyano complex is in the (IV) state and it is diamagnetic.

The molecular weight determination by the elevation of boiling point method with water as solvent gave an apparent mol. wt. of 132. This clearly shows the formation of two ions from $KMo(CN)_5$ and the results of conductance measurements tend to confirm the existence of an $[Mo(CN)_5]^-$ ion.

The coordination number of the molybdenum atom thus appears to be 5.

If single bonding between the molybdenum and cyanide occurs the possible electronic arrangements for bonding in this diamagnetic compound are d^4s

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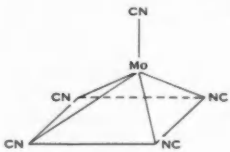
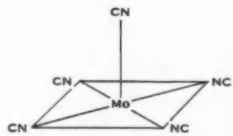
d^3sp, d^2sp^2, and dsp^3. Either a bipyramidal or tetragonal pyramidal arrangement is possible. However, the complex $KMo(CN)_5$ is a very stable substance and its behaviour is in keeping with the " inner orbital " type of complex (Taube 1952). It may therefore be expected that the bond orbitals involved would be d^4s and not d^3sp, d^2sp^2, or dsp^3. With the filling of the first $4d$ orbitals by the paired electrons of the molybdenum(IV) the next available orbitals are four $4d$ and one $5s$ and these would be used for bonding with the five cyanide groups.

Possible spatial arrangement for d^4s bonds are shown in Figures 1 (*a*) and (*b*).



(a)

Fig. 1(*a*)



(b)

Fig. 1(*b*)

Infra-red spectroscopy of $KMo(CN)_5$ showed no evidence of bridging of the cyanide groups (Irving, personal communication).

Partial double-bond character of the metal-carbon bond appears in cyanide complexes of other transitional elements such as $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, $[Mn(CN)_6]^{4-}$, $[Ni(CN)_4]^{2-}$, and $[Cr(CN)_6]^{4-}$ (Pauling 1944).

Double bonding may occur in cyanide complexes where there is evidence for the existence of d_π——p_π bonding with a penultimate d_π orbital. The stability and inertness of the $[Mo(CN)_5]^-$ ion suggests some double-bonding character besides an " inner orbital " type of formation and the filled $4d$ orbital could in fact give rise to some small π bonding. However, the structure of $KMo(CN)_5$ cannot be solved without recourse to an X-ray study.

The potassium in $KMo(CN)_5$ cannot be replaced by elements such as copper, cobalt, cadmium, or manganese as occurs with the octacyanide.

Young (1932) stated that the black cyanide $K_4Mo(CN)_7.2H_2O$ is unstable and reverts to the yellow octacyanide $K_4Mo(CN)_8$ in the presence of moist air. Further investigation into this behaviour has shown that the black cyanide oxidizes to give the white cyanide $KMo(CN)_5$ and potassium hydroxide together with the yellow cyanide $K_4Mo(CN)_8$ according to the equation

$$3K_4Mo(CN)_7.2H_2O+\tfrac{3}{4}O_2\rightarrow 2K_4Mo(CN)_8+KMo(CN)_5+3KOH+\tfrac{9}{2}H_2O.$$

Conductance measurements and pH determinations were made whilst passing a stream of air through a solution of the black cyanide. In these circumstances the rate of hydrolysis increased and the pH increased to 11 after 80 min. This pH value of 11 is commensurate with that expected by the formation of the KOH according to the above equation (the experimental values are presented in Section III (*b*)). The weight of the white cyanide formed as a decomposition product of the black cyanide approximated the theoretical yield.

Repeated attempts to prepare $K_4Mo(OH)_4(CN)_4.4H_2O$ and $K_3Mo(OH)_3(CN)_4.3H_2O$ according to Bucknall and Wardlaw's method failed; the results of analysis showed the preparation to be $K_4MoO_2(CN)_4$. Another procedure given in Section III also produced the brown $K_4MoO_2(CN)_4$. This brown cyanide does not appear to be an anhydrous form of Bucknall and Wardlaw's preparation as it does not become red with water. It does, however, turn red when moistened with potassium hydroxide solution.

When the brown cyanide $K_4MoO_2(CN)_4$ is heated at 120 °C there is no apparent change, but when it was heated to 600 °C (approx.) the compound turned white. Some of this white product was found to be $KMo(CN)_5$ and its weight approximated the theoretical yield expected according to the equation

$$2K_4MoO_2(CN)_4+\tfrac{1}{2}O_2\rightarrow KMo(CN)_5+3KCN+K_2O+K_2MoO_4.$$

Table 1 gives the magnetic susceptibilities, the probable bond orbitals used, and the suggested shape of the white and brown cyanides.

TABLE 1

PHYSICAL PROPERTIES OF MOLYBDENUM CYANIDE COMPLEXES

Complex	Colour	Bond Orbitals	Suggested Shape	Magnetic Measurements	
				Calc. (B.M.)	Expt.
Potassium pentacyano molybdate(IV)	White	$4d^45s$	Tetragonal pyramid	0	$\chi\times10^6$ —0·127
Potassium tetracyano dioxo molybdate(IV)	Brown	$4d^45s5p^3$	Dodecahedron	0	—0·046
Potassium heptacyano molybdate(III)	Black	—	—	0	0

III. EXPERIMENTAL

(a) *Preparations*

(i) *Potassium Pentacyano Molybdate(IV).*—Equal parts of MoO_3 and KCN were weighed. The MoO_3 was dissolved in the aqueous solution of KCN. The solution was filtered and concentrated by boiling. This concentrate was allowed to crystallize (over a 3 weeks period) and white crystals separated, which were redissolved in hot water and reprecipitated by crystallization (Found: Mo, 36·4; CN, 49·1; K, 14·8%. Calc. for $KMo(CN)_5$: Mo, 36·3; CN, 49·3; K, 14·7%).

The pentacyano complex is a white crystalline substance, not very soluble in water, insoluble in the usual organic solvents; soluble in KCN solution. On heating, the crystals changed colour to brown, and then gave a yellow melt which, on cooling, reverted to the original white crystals.

(ii) *Potassium Tetracyano Dioxo Molybdate(IV).*—MoO_3 (10 g) and KCN (20 g) were mixed by grinding together in an agate mortar. To this mixture was added water (60 g) over a period of 2 hr. The solution was refluxed 3 hr and gave a yellowish brown coloured solution. This solution was then evaporated until saturated and on crystallization red crystals formed. These crystals were purified by repeated leaching with 70 : 30 ethanol and water mixture. The final product was washed with absolute ethanol and dried at 40 °C. The colour of the dried product was brown (Found: Mo, 24·5; CN, 27·0; K, 39·9%. Calc. for $K_4MoO_2(CN)_4$: Mo, 24·7; CN, 26·9; K, 40·1%).

Second preparation of $K_4MoO_2(CN)_4$: Following Bucknall and Wardlaw's method for $K_4Mo(OH)_4(CN)_4.4H_2O$, 10% MoO_3 (150 ml) in 3N HCl was electrolysed (using a mercury cathode and platinum anode) to the Mo(V) state. The electrolysed solution was concentrated under reduced pressure at 60–70 °C to about 15 ml. On the careful addition of a concentrated solution of KOH, the brown hydroxide of quinquevalent molybdenum was obtained. On addition of the theoretical amount of KCN (27 g), as a saturated solution, the hydroxide slowly dissolved. This solution was concentrated under reduced pressure at 70 °C and ethanol was added when a precipitate formed which was red while in contact with the mother liquor. This precipitate was washed with absolute alcohol and became brown on drying (Found: Mo, 24·7; CN, 26·9%).

The tetracyano dioxo complex $K_4MoO_2(CN)_4$ is a brown substance. It is very soluble in water giving a yellowish brown solution. It does not melt, but decomposes with heat to give a white product which is sparingly soluble in cold water, $KMo(CN)_5$.

(iii) *Potassium Heptacyano Molybdate(III):Preparation 1.*—K_3MoCl_6 (2 g), KCN (3·5 g), and air-free water (20 ml) were introduced into a reaction vessel and an inert nitrogen atmosphere was maintained for 18 hr. The red solution changed to brown and a precipitate formed; the solution became black and ultimately all the precipitate dissolved to give a dark red-brown solution. Air-free ethanol was added and a black precipitate formed. This was washed by decantation several times with absolute ethanol, filtered, and again washed with absolute ethanol. A nitrogen atmosphere was maintained throughout the process.

Second Preparation of $K_4Mo(CN)_7.2H_2O$. $MoCl_3$ solution (250 ml; 250 g H_2MoO_4/l) in HCl were added to KCN (36 g). This solution was placed in an electrolytic cell and electrolysed for 18 hr using a mercury cathode and a platinum anode. Absolute ethanol, air-free and saturated with hydrogen, was introduced under pressure into the cell, a black precipitate formed from a dark reddish brown solution. The black precipitate was tapped off from the bottom of the electrolytic cell into air-free absolute ethanol, washed by decantation with absolute ethanol, and filtered and again washed with absolute ethanol. A hydrogen atmosphere was maintained except for the final filtration (Found: Mo, 20·4; CN, 38·5; K, 33·3%. Calc. for $K_4Mo(CN)_7.2H_2O$: Mo, 20·4; CN, 38·7; K, 33·2%).

The black heptacyano complex is soluble in water to give a brown solution; insoluble in ethanol; it changes to the yellow and white cyanides in the presence of moist air.

(iv) *Oxidation of the Black Heptacyanide.*—A fresh preparation of the dry black cyanide was left exposed to air for about 2 hr. Potassium hydroxide and the yellow $K_4Mo(CN)_8$ complex were leached with cold water, leaving a white residue (Found: Mo, 36·5; CN, 49·0%. Calc. for $KMo(CN)_5$: Mo, 36·3; CN, 49·3%).

(v) *Heating the Brown Tetracyano Dioxo Complex.*—$K_4MoO_2(CN)_4$ (0·65 g) was heated to about 600 °C. The original substance changed colour from brown to white. This white substance was leached with cold water, and the white residue after leaching weighed 0·22 g. The water-soluble portions were alkaline (Found: K, 14·6; Mo, 36·2; CN, 49·0%. Calc. for $KMo(CN)_5$: K, 14·7; Mo, 36·3; CN, 49·3%).

(b) *Conductivity Measurements*

Molecular Conductivity in Reciprocal Ohms; 25 °C

$K_4MoO_2(CN)_4$			
Mol. cond.			
M/1000 ..	354	354	354
Time (min) ..	3	5	10
$KMo(CN)_5$			
Mol. cond.			
M/500	157	157	157
Time (min) ..	6	12	30
$K_4Mo(CN)_7.2H_2O$			
Mol. cond.			
M/1000 ..	474	510	512
Time (min) ..	3·5	45	90

Molecular Conductivity in Reciprocal Ohms ; 25°C (Continued)

$K_4Mo(CN)_7.2H_2O$

Mol. cond. M/1000	..	520	520	520	520	520
Time (min)	..	1	2	3	4	5
pH ..	..	9·26	9·32	9·34	9·35	9·46
Mol. cond. M/1000	..	—	—	—	—	560
Time (min)	..	10	15	20	25	80
pH ..	..	10·23	10·84	10·92	10·93	11·0

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THE CATALYTIC HYDROGENATION OF BENZENE AND TOLUENE OVER EVAPORATED FILMS OF NICKEL AND TUNGSTEN

By J. R. Anderson*

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Summary

In the vapour-phase hydrogenation of benzene and toluene over evaporated films of nickel and tungsten there is some poisoning of the catalyst surface by adsorbed hydrocarbon residues, resulting in falling rates of hydrogenation. Activation energies and frequency factors are obtained from initial rates. On poisoned nickel, rates pass through a maximum at about 90 °C. The rate and extent of poisoning increase with temperature. Some *cyclo*hexene is sometimes formed during the hydrogenation of benzene over nickel. The hydrogenation of *cyclo*hexene over nickel is extremely rapid but strongly inhibited by benzene. On a benzene poisoned nickel surface *cyclo*hexene disproportionates to benzene and *cyclo*hexane, and this reaction also occurs to a small extent during hydrogenation of *cyclo*hexene.

I. Introduction

The vapour-phase hydrogenation of benzene has been studied over a number of metallic catalysts. A summary of the early work is given by Berkman, Morrell, and Egloff (1940). With the demonstration of the inactivity of pure copper by Ipatieff, Corson, and Kurbatov (1939) and of silver by Anderson and Kemball (1956), activity appears to be limited to the transition metals or their alloys, at least at low temperatures. However, few experiments have been conducted over clean metal surfaces such as are produced in evaporated films. Beeck and Ritchie (1950) have very briefly reported some results over films of nickel and iron, and recently, Anderson and Kemball (1956) have described hydrogenation and exchange over (mainly) films of palladium and platinum.

The work of Beeck and Ritchie (1950) and, more recently, Jenkins and Rideal (1955) on nickel films has emphasized the importance of strongly held hydrocarbon residues in reducing the effective area available in the hydrogenation of ethylene. It was of interest in the present work to assess the importance of poisoning in the hydrogenation of benzene and toluene over films of nickel and tungsten. Some experiments were also done with *cyclo*hexene to compare the behaviour of a cyclic olefin.

II. Experimental

The apparatus consisted of a reaction vessel (200 ml), on the inner surface of which films of metal could be deposited by evaporation, connected to (*a*) an all-glass diaphragm gauge for measuring the pressure to $\pm 0 \cdot 05$ mm Hg, (*b*) a stopcock and line through which samples could be transferred to a gas-liquid

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partition chromatographic (G-L.P.C.) column, (*c*) a stopcock to the vacuum line and gas-handling system. The reaction vessel was demountable by a water-cooled ground-glass joint. The reaction was followed by measuring the change in pressure, and in a number of experiments the products were analysed by G-L.P.C. Reproducible evaporated metal films were prepared in a manner described by Kemball (1951). The film weights were in the range 5–10 mg. The gas mixture was always admitted to the reaction vessel at 0 °C, and at a partial pressure of hydrocarbon of 6·88 mm, and the reaction vessel was estimated to contain $4 \cdot 8 \times 10^{19}$ hydrocarbon molecules. The ratio of hydrogen to hydrocarbon was either 3/1 or 6/1. Cylinder hydrogen was purified by passaging it over reduced pure copper at 400 °C and by its passage through liquid-air traps. " Analar " grade benzene, toluene, and *cyclo*hexene were used without further purification, except for the removal of dissolved air. Each gas mixture was used at one temperature only.

Analysis by G-L.P.C. used a column, 290 cm long, of polyethylene glycol phenyl ether supported on pulverized firebrick (44–60 mesh) operated at 80 °C. A column of only half this length is adequate for the separation of benzene from *cyclo*hexane (Anderson and Napier 1956), but the increased length is necessary for the analysis of mixtures containing, in addition, *cyclo*hexene. To obtain sufficient sensitivity it was necessary to use hydrogen as the carrier gas and to use all the gas in the reaction vessel in a single analysis. The gas mixture was transferred from the reaction vessel to the column by a Toepler pump.

III. Results

Let p_{H_2} be the hydrogen pressure at time t, p_{HC} the hydrocarbon pressure at time t, and p^0_{HC} the hydrocarbon pressure at zero time, then if the rate of hydrogenation is proportional to $p_{H_2} \times p^0_{HC}$, a plot of $\ln p_{HC}/p^0_{HC}$ against time should be linear for a 3/1 mixture, and for a 6/1 mixture a plot of $\ln (p_{HC}+p^0_{HC})/2p^0_{HC}$ should be linear. Most of the experimental results when plotted in this way showed an initial decrease in rate followed by a more or less linear plot (cf. curves (*b*) and (*c*) of Fig. 1). The exceptions are mentioned below. As will be shown later, the observed decrease in rate cannot be accounted for by a reasonable modification of the dependence of reaction rate on gas pressure.

Using the stoichiometric ratio of hydrogen to benzene (3/1), the rates of all reactions tended to decrease with time. At 120 and 170 °C over nickel, the rate of decrease in velocity was too rapid for the rate of initial reaction to be measured before all reaction ceased. Pretreatment of a nickel film at 110 °C for 10 min with benzene vapour at 7·5 mm pressure temporarily inhibited the reaction of a 3/1 mixture at 87 °C, but similar pretreatment at 40 °C gave no inhibition (Fig. 2), although the initial rapid fall in rate was eliminated.

Using a hydrogen to benzene ratio of 6/1, the decrease in reaction rate was still evident, but reaction could now be observed at 120 °C. Pretreatment of a nickel film with 30 mm of hydrogen for 5 min at 120 °C resulted in an observable reaction with a 3/1 mixture at 120 °C, but similar pretreatment at 43 °C did not prevent the fall in rate with a 6/1 mixture at 45 °C. Over tungsten with a 6/1 mixture the reaction was very rapid at 0 °C, with a half-life of about 2 min.

With toluene (3/1) over nickel, reaction was observed up to 131 °C and over tungsten the behaviour resembled that of benzene.

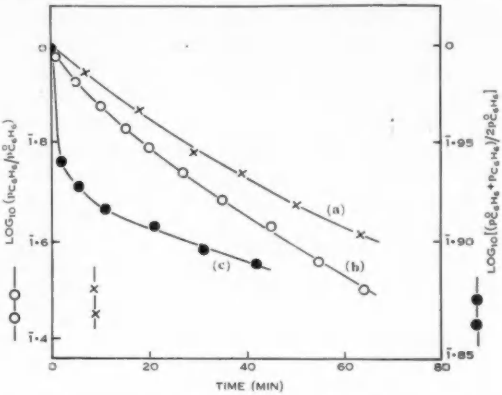

Fig. 1.—Hydrogenation of benzene: (*a*) 3/1 mixture over 5·1 mg Ni at 45 °C; (*b*) 3/1 mixture over 7·7 mg W at 0 °C; (*c*) 6/1 mixture over 8·1 mg Ni at 119 °C.

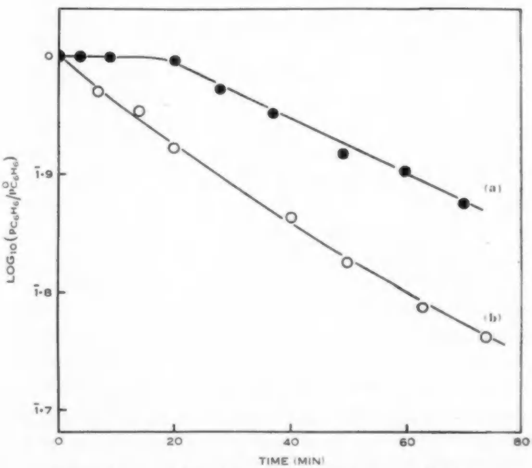

Fig. 2.—Hydrogenation of benzene, 3/1 mixture, at 87 °C over: (*a*) 6·0 mg Ni pretreated with 7·5 mm benzene vapour at 110 °C for 10 min; (*b*) 6·8 mg Ni pretreated with 7·5 mm benzene vapour at 40 °C for 10 min.

*cyclo*Hexene and hydrogen (1/1) reacted with great rapidity over nickel at 0 °C, the entire reaction being complete in less than 1 min. Because of the reduced vapour pressure of *cyclo*hexene at low temperatures, experiments could

not be done at a sufficiently low temperature for accurate rate measurements to be made.

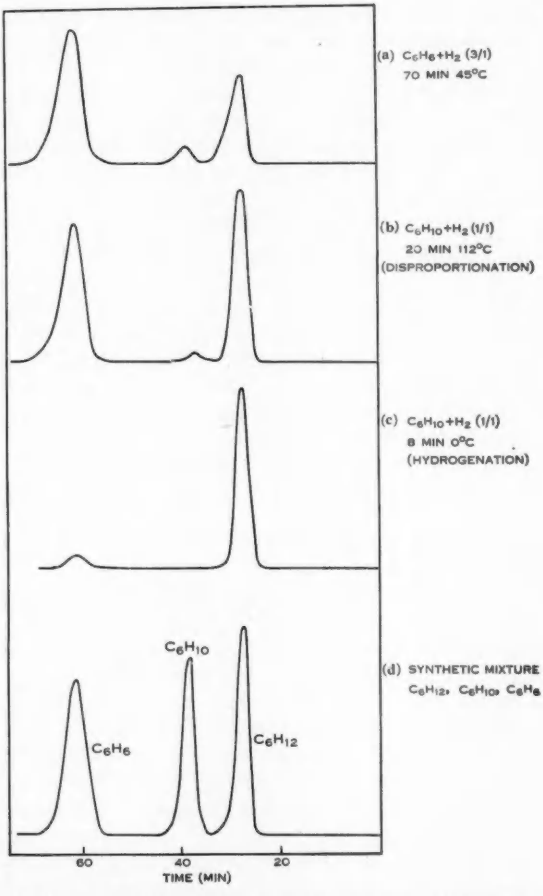

Fig. 3.—Gas-liquid partition chromatograms from (*a*) hydrogenation of benzene, 3/1 mixture, over 6·0 mg Ni for 70 min at 45 °C ; (*b*) reaction at 112 °C for 20 min of mixture of 8·7 mm *cyclo*hexene, 9·3 mm hydrogen, over 6·0 mg Ni pretreated with mixture of 7·5 mm benzene and 20 mm hydrogen at 112 °C for 10 min ; (*c*) hydrogenation of *cyclo*hexene, 1/1 mixture, over 6·5 mg Ni at 0 °C for 8 min ; (*d*) synthetic mixture of *cyclo*hexane, *cyclo*hexene, and benzene.

Two rate constants are presented in Table 1 for each reaction : the initial rate and the rate after an arbitrary period of 30 min.

Analysis by G-L.P.C. of the products from the reaction of hydrogen and benzene (3/1) over nickel at 45 °C showed the presence of appreciable quantities of *cyclo*hexene as well as *cyclo*hexane.* The chromatogram shown in Figure 3 (*a*) was taken after reacting for 70 min over 6·0 mg of nickel, the product contained approximately 19 per cent. *cyclo*hexene. Reaction for 30 min under similar conditions gave about the same proportion of *cyclo*hexene. No *cyclo*hexene was found from a similar reaction at 91 °C for 78 min. After pretreatment of nickel with benzene at 110 °C (no hydrogen added) as described previously, the gas in the reaction vessel contained about 40 per cent. *cyclo*hexane but no *cyclo*hexene.

A mixture of hydrogen and benzene (3/1), together with an amount of *cyclo*hexene equal to that of the benzene, was reacted at 112 °C on a nickel film which had been pretreated at 112 °C either with benzene as described above or with a 3/1 hydrogen-benzene mixture for 10 min. There was no change in pressure but analysis of the reaction mixture after 15 min showed the almost complete disappearance of *cyclo*hexene and the formation of substantial quantities of both benzene and *cyclo*hexane. Experiments on a similarly pretreated nickel film using a mixture of hydrogen and *cyclo*hexene (1/1) gave a similar result (Fig. 3 (*b*)).

Analysis of the reaction product from the hydrogenation of *cyclo*hexene on nickel at 0 °C showed the presence of about 8 per cent. benzene, the rest being *cyclo*hexane (Fig. 3 (*c*)).

IV. Discussion

Numerous experiments (Kemball 1953 ; Anderson and Kemball 1954) have shown that in the presence of a chemisorbed gas sintering is negligible with nickel and tungsten films below at least 190 °C, and that the rate of diffusion of the reactants in this type of apparatus and at the pressures which have been used is not likely to limit the rate of reaction. There is a great deal of evidence (cf. Eley 1949) to show that over transition metal catalysts, the rate of hydrogenation of benzene is independent of benzene pressure. Further, the results in Table 1 show that over nickel at 45 °C the initial rate of hydrogenation is approximately proportional to $(p_{H_2})^1$, in agreement with previous work (cf. Eley 1949). Therefore, it is very unlikely that the fall in reaction rate can be accounted for by making a different set of assumptions regarding the dependence of the rate on gas pressure, particularly since to fit the results the exponents of the pressures would have to be increased. Moreover, in many cases (e.g. curve (*c*), Fig. 1) the fall in rate is far too great to be accounted for by such means. The decreasing rates of hydrogenation with time are clearly due to progressive poisoning of the catalyst surface by adsorbed hydrocarbon residues. Calculations from free energy data (Rossini 1947) show that failure to react at 170 °C cannot be due to adverse equilibrium conditions.

Owing to the difficulty in measuring initial rates, the figures given in Table 1 are approximate, particularly at higher temperatures. Except at 45 °C on nickel, the rates of hydrogenation had become nearly constant after 30 min and

* The possibility of the formation of *cyclo*hexene was suggested to the author during a discussion with Professor C. Kemball.

the poisoning had reached an equilibrium value. The higher the temperature, the more rapid was the approach towards poisoning equilibrium, showing that the poisoning was an activated reaction. Assuming that hydrogenation occurs only on that part of the surface left uncovered by residues, the proportion of the surface covered after 30 min may be deduced (Table 1). Except for nickel at 45 °C, the coverages approximate to equilibrium values. They show that the extent of equilibrium poisoning increases with temperature. Figure 2 shows that on nickel

TABLE 1

RATES OF HYDROGENATION

Mixture	Rate (% hydrocarbon/min 10 mg)		Percentage Surface Poisoned After 30 min
	Initial	After 30 min	
(3/1), benzene, Ni			
45 °C	0·9	0·5	45
89 °C	~2	1·1	45
120, 170 °C ..	—	0	(100)
(6/1), benzene, Ni			
45 °C	2·0	1·0	50
90 °C	~10	4·5	55
96 °C	~13	5·3	60
119 °C	~24	0·6	97
(3/1), toluene, Ni			
45 °C	0·42	0·3	29
84 °C	3·5	0·5	86
107 °C	~6	0·3	95
131 °C	—	0·1	—
(3/1), benzene, W			
0 °C	~5	2·0	60
35 °C	~6	2·1	65
(3/1), toluene, W			
0 °C	~3	0·7	79
36 °C	~5	0·7	86
(3/1), benzene, 120 °C on Ni pretreated with H_2 at 120 °C ..	—	0·53	—
(6/1), benzene, 45 °C on Ni pretreated with H_2 at 43 °C ..	1·0	0·6	40

the poisoning is reversible at least up to 110 °C. The rate of the reaction, which set in at 87 °C after the inhibition caused by poisoning at 110 °C, was approximately the same as the equilibrium rate (Table 1). The extent of poisoning was dependent on the hydrogen to hydrocarbon ratio since on nickel at 120 °C after 30 min a reaction was observed with a 6/1 but not with a 3/1 mixture of hydrogen and benzene. As a result of poisoning, the rates measured after 30 min pass through a maximum at about 90 °C. The self-hydrogenation of benzene and the

activation energy of the poisoning process support the idea that poisoning is due to dissociative chemisorption of the aromatic molecules.

Where sufficient data are available, the activation energies and frequency factors for hydrogenation over nickel are given in Table 2. The value of 7·3 kcal mole^{-1} for benzene is to be compared with 8·7 kcal mole^{-1} found by Beeck and Ritchie (1950) for this catalyst. From the data given by these authors the rate of hydrogenation of benzene over nickel at 57 °C may be computed for the same reactant pressures as used in the present paper (for a 3/1 mixture). The actual value depends somewhat upon the way in which the rate is assumed to vary with hydrogen pressure. Using the result found in the present work that the rate is proportional to $(p_{H_2})^1$, the computed rate is 0·055 per cent. benzene/min 10 mg, while using the result quoted by Beeck and Ritchie that the rate is proportional to $(p_{H_2})^{0\cdot 5}$ the computed rate is 0·16 per cent. benzene/min 10 mg. In either case, a comparison with the present results suggests that

TABLE 2

ACTIVATION ENERGIES AND FREQUENCY FACTORS FROM INITIAL RATES OF HYDROGENATION

Mixture	Activation Energy (kcal mole^{-1})	Frequency Factor (mol/sec 10 mg)
Benzene, 6/1	7·3	$1\cdot 8\times 10^{21}$
Toluene, 3/1	9·6	18×10^{21}

Beeck and Ritchie were working with considerably poisoned films. This is reasonable since they had no hydrogen in excess of the stoichiometric quantity. Since it has been shown in the present paper that poisoning tends to become less serious the higher the hydrogen to benzene ratio, this may be one reason why Anderson and Kemball (1956) did not observe any poisoning effect in the reaction between benzene and a large excess of deuterium (20/1) over films of palladium and platinum. It is clear that any attempt to correlate hydrogenation activity with catalyst structure should use either initial reaction rates or else make allowance for the effect of poisoning.

The exchange of benzene with deuterium over nickel which proceeds rapidly at −45 °C involves the adsorption of benzene as phenyl and phenylene radicals (Anderson and Kemball 1956). The much greater difficulty of hydrogenation suggests for this reaction a different mode of adsorption, probably by double-bond opening.

The production of *cyclo*hexene by the catalytic hydrogenation of benzene does not appear to have been previously recorded.* The equilibrium constants (at 45 °C) for the production of *cyclo*hexene ($K=5\cdot 8\times 10^{8}$) and *cyclo*hexane ($K=5\cdot 6\times 10^{14}$) are both highly favourable, so that the product will depend on the selectivity of the catalyst. Anderson and Kemball (1956) did not find any

* The two instances quoted by Berkman, Morrell, and Egloff (1940, p. 831) are incorrect : in the reference the production of *cyclo*hexene is not claimed.

(deutero)*cyclo*hexene in the product of their reactions over palladium and platinum, and this may be due not only to the nature of the catalyst, but also to the large excess of deuterium.

Although on nickel even at 0 °C the hydrogenation of *cyclo*hexene is extremely rapid, this reaction is very strongly inhibited by the presence of a substantial quantity of benzene which must be much more strongly adsorbed. *cyclo*Hexene was proposed by Zelinsky (1925) as a transitory intermediate in the hydrogenation of benzene.

The disappearance of *cyclo*hexene with the production of benzene and *cyclo*hexane is probably due to the disproportionation

$$3C_6H_{10} \rightarrow C_6H_6 + 2C_6H_{12}, \quad \ldots\ldots\ldots\ldots\ldots \quad (\mathbf{1})$$

which was also observed by Zelinsky (1925) and Zelinsky and Pawlow (1933) for pure *cyclo*hexene over palladium black, and by Shcheglova and Kagan (1949) over pumice-supported platinum. The composition of the products and absence of pressure change agree with this reaction. Calculation from free energy data (Rossini 1947 ; Rossini, Epstein, and Pitzer 1949) shows that, of the possible disproportionation reactions, (**1**) represents the only process sufficiently favourable thermodynamically at 112 °C. Under the present experimental conditions the reaction went to completion in about 10 min. The absence of a pressure change shows that no direct hydrogenation occurred. Absence of *cyclo*hexene from the gas phase during the hydrogenation of benzene may, in general, be due to either (i) further hydrogenation before leaving the surface (i.e. lack of the appropriate surface groups to give *cyclo*hexene on desorption), or (ii) rapid disproportionation. It is expected that (i) may be the limiting factor in the presence of a large excess of hydrogen, while (ii) may occur at higher temperatures.

The formation of a small quantity of benzene during the hydrogenation of *cyclo*hexene (at a temperature where the rate of hydrogenation of benzene is negligibly slow) shows that during the process reaction (**1**) occurs to a small extent.

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HEATS OF MIXING

III. ACETONE AND ALCOHOL SOLUTIONS

By I. Brown* and W. Fock*

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Summary

The heats of mixing at 45·00 °C have been measured at intervals over the whole concentration range for the following systems: acetone+benzene, acetone+carbon tetrachloride, acetone+acetonitrile, acetone+nitromethane, *n*-propanol+benzene, and *n*-butanol+benzene. The heats of mixing are discussed in the light of the authors' earlier results for similar systems.

I. Introduction

The heats of mixing of a number of systems containing polar components are being measured to permit the excess entropy of mixing to be calculated with greater accuracy than can be obtained from free energy data alone. References are given below for published heats of mixing for some of these systems at temperatures of 20 °C or below, but these are not suitable for the calculation of excess entropies from free energy data which were measured at 45 °C. The results given here form part of a programme to provide experimental thermodynamic data for testing statistical theories of polar non-electrolyte solutions.

II. Apparatus and Methods

The apparatus used was that described by Brown and Fock (1955) and the method of operation was that given by those authors (Brown and Fock 1956). With the techniques used no latent heat effects occur due to changes in vapour composition on mixing.

III. Components

Acetone was purified by the method of Thirion and Craven (1952) and the alcohols by careful fractional distillation at high reflux ratios in the column described by Brown and Ewald (1951). The other liquids were purified by the methods described by Brown and Smith (1954, 1955). The density and refractive index of each purified liquid were measured as criteria of purity; the values obtained are shown in Table 1.

IV. Results

The results obtained are given in Tables 2 to 7, where x_1 is the mole fraction of the first-mentioned component and H_x^M, expressed as J/mol of mixture, is the heat of mixing. A check was made of the experimental data by plotting

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TABLE 1

PHYSICAL PROPERTIES OF COMPONENT LIQUIDS

Liquid	$n_D^{25\cdot00}$	$d_4^{25\cdot00}$
Acetone	1·35598	0·78501
Acetonitrile	1·34153	0·77662
Nitromethane	1·37968	1·13062
Benzene	1·49800	0·87362
Carbon tetrachloride	1·45739	1·58452
n-Propanol	1·38314	0·79959
n-Butanol	1·39731	0·80577

H_x^M/x_1x_2 against x_1 as recommended by Korvezee, Ruiter, and Stuyts (1953), for all systems the points were on smooth curves. The experimental errors were estimated to be from 2 to 3 per cent.

TABLE 2

HEAT OF MIXING ACETONE+BENZENE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·157	116	0·594	152
0·279	147	0·602	148
0·488	159	0·604	145
0·493	158	0·788	108

For the system acetone+benzene heat of mixing data are given at 30 °C by Möbius (1955), who also gives one value at 20 °C. A value at one concentration at 20 °C is given by Timofiev (1905). No reliable estimates could be calculated from published free energy data.

TABLE 3

HEAT OF MIXING ACETONE+CARBON TETRACHLORIDE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·132	256	0·619	196
0·294	317	0·620	189
0·493	266	0·799	106
0·496	263	0·839	83
0·615	197		

For the system acetone+carbon tetrachloride the only value for the heat of mixing is a single measurement by Timofiev (1905). No reliable estimates of the heat of mixing for this system could be obtained from free energy data even using the comparatively accurate data of Severns *et al.* (1955) at 50 °C and

TABLE 4

HEAT OF MIXING ACETONE + ACETONITRILE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·083	—22	0·465	—106
0·155	—47	0·467	—108
0·192	—57	0·759	—81
0·366	—96	0·890	—41
0·373	—99		

TABLE 5

HEAT OF MIXING ACETONE + NITROMETHANE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·081	—27	0·465	—159
0·191	—71	0·467	—159
0·363	—134	0·681	—163
0·367	—136	0·848	—107
0·461	—154		

TABLE 6

HEAT OF MIXING *n*-PROPANOL + BENZENE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·100	921	0·596	1084
0·218	1264	0·611	1052
0·479	1247	0·822	537
0·483	1264		

TABLE 7

HEAT OF MIXING *n*-BUTANOL + BENZENE AT 45·00 °C

x_1	H_x^M (J/mol)	x_1	H_x^M (J/mol)
0·082	865	0·550	1235
0·190	1254	0·551	1241
0·438	1393	0·804	635
0·439	1383		

that of Brown and Smith (1957) at 45 °C as the estimated errors were of the same order as the heats of mixing themselves.

No information seems to be available for the systems of acetone + acetonitrile or acetone + nitromethane.

Published heats of mixing are given for the system *n*-propanol + benzene at 15 °C by Schmidt (1926), at 20 °C by Pahlke (1935), and a single value by Timofiev.

Data on the heat of mixing of the system *n*-butanol + benzene at 20 °C are given by Perrakis (1925) and Pahlke (1935).

V. Discussion

The data given here for mixtures of acetone with carbon tetrachloride and with benzene, together with those for the corresponding systems containing acetonitrile and nitromethane (Brown and Fock 1956), form two interesting series of measurements. The heats of mixing for the carbon tetrachloride systems are all more positive than those for the corresponding benzene systems. This is probably due to the polar molecules interacting more strongly with the π-electrons of the benzene molecules than with the electrons of the carbon tetrachloride molecules. Similar conclusions on the interactions of ethanol with benzene and with carbon tetrachloride were reached by Brown, Fock, and Smith (1956).

In the series of solutions with carbon tetrachloride the heat of mixing becomes less positive in the order: nitromethane, acetonitrile, acetone; the same sequence is found for the series of benzene solutions. This is not the order of their dipole moments, which are respectively 3·44, 3·96, and 2·87 D, neither is it in the order of the difference from unity of the "g" factor of Oster and Kirkwood (1943).

The negative heats of mixing for acetone with nitromethane and with acetonitrile show that the electrostatic interaction between pairs of the unlike molecules is stronger than that between the like molecules; part of this effect may be due to weak hydrogen bonds between the oxygen of acetone and the positive ends of the nitromethane and acetonitrile molecules. The heat of mixing for the system acetone + propionitrile at 20 °C is also negative (Thacker and Rowlinson 1954). For the binary system nitromethane + acetonitrile, where the dipole moments and molar volumes of the components are very similar, it was shown by Brown and Fock (1956) that both the heat and excess free energy of mixing are very close to zero.

For solutions in benzene of aliphatic alcohols the variation in H_x^M with the size of the alcohol molecule was discussed by Brown, Fock, and Smith (1956), who showed that the heat and excess entropy of mixing became rapidly more positive in the series of benzene solutions containing methanol, ethanol, and *iso*propanol. The new data given here, together with published values at lower temperatures (Perrakis 1925; Schmidt 1926; Pahlke 1935; Williams, Rosenberg, and Rothenberg 1948; Scatchard *et al.* 1952; Tsao 1953; Thacker and Rowlinson 1954) show more clearly the effect of the size of the alcohol molecule. These data are shown in Figure 1, where the maximum in the H_x^M curve is plotted against the number of carbon atoms in the alcohol molecule.

These maxima all occur at mole fractions of alcohol between 0·28 and 0·48. Values at 20 °C are shown as triangles and those at 45 °C as circles, open symbols are used for normal alcohols and closed for *iso*propanol. It can be seen that, while the size of the normal alcohol has only a small influence in the maximum value of H_x^M, the maxima for *iso*propanol solutions are considerably higher than those for *n*-propanol. Probably this means that more alcohol-alcohol hydrogen

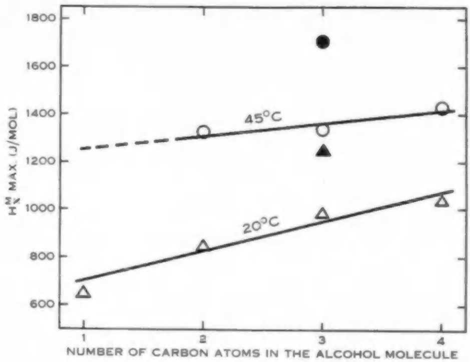

Fig. 1.—Heats of mixing, benzene+alcohol systems. ○ and △ Normal alcohols. ● and ▲ *iso*Propanol.

bonds are broken at a given concentration in *iso*propanol solutions than in *n*-propanol solutions (cf. Brown, Fock, and Smith 1956). It is intended to measure values of the excess free energy of mixing for the system *n*-propanol+benzene. It will then be possible to calculate the excess entropy of mixing which may help to explain the difference in behaviour between *n*-propanol and *iso*propanol in benzene solution.

VI. Acknowledgments

The authors wish to thank Mr. J. A. Barker for discussions of the results.

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LIQUID–VAPOUR EQUILIBRIA

VIII. THE SYSTEMS ACETONE+BENZENE AND ACETONE+CARBON TETRACHLORIDE AT 45 °C

By I. Brown* and F. Smith*

[*Manuscript received May* 13, 1957]

Summary

The liquid-vapour equilibrium data are given for the systems acetone+benzene and acetone+carbon tetrachloride at 45·00 °C. These data are used to calculate the excess free energy of mixing for these systems.

I. Introduction

The isothermal liquid-vapour equilibria for the system acetone+benzene have been determined at 25 and 35 °C by Litvinov (1940) and measurements at atmospheric pressure have been made by Soday and Bennett (1930), Reinders and De Minjer (1940), Othmer (1943), Tallmadge and Canjar (1954), Canjar, Horne, and Rothfus (1956), and Kranich *et al.* (1956). For acetone+carbon tetrachloride, liquid-vapour equilibrium data have been measured at 0 °C by Gerrits (1904), at 50 °C by Severns *et al.* (1955), and at 760 mm Hg by Acharya and Rao (1953) and at 300, 450, and 760 mm Hg by Bachman and Simmons (1952). The present measurements were made in order to obtain values of the isothermal excess free energy of mixing at 45 °C for comparison with values obtained previously at this temperature for other systems containing polar components.

II. Experimental

(*a*) *Apparatus*

The liquid-vapour equilibrium and vapour pressure measurements were made using the equilibrium still described by Brown (1952); pressure measurements were made by the methods of Brown and Ewald (1950). Temperatures were measured with a calibrated Myer type platinum resistance thermometer and a calibrated Mueller bridge. The emergent stem of the resistance thermometer was maintained within less than 1 °C of the temperature being measured by means of a small electrically-heated tube, fitted with a differential thermocouple connected to a galvanometer. Temperatures were measured to $\pm 0{\cdot}002$ °C and are recorded to 0·01 °C. Liquid and vapour samples were analysed by refractive index measurements using a Hilger-Chance precision refractometer maintained at $25{\cdot}00 \pm 0{\cdot}01$ °C.

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(b) *Purification and Properties of Components*

Benzene was purified by the method described by Brown and Ewald (1951) and carbon tetrachloride by that of Barker, Brown, and Smith (1953). Previously, distilled acetone was dried by a chemical method (Brown and Fock 1955, 1957), with a resulting density of d_4^{25} 0·78501. For the present work, acetone was purified and dried by careful fractional distillation at a reflux ratio

TABLE 1

PHYSICAL PROPERTIES OF COMPONENTS

Property	Acetone	Benzene	Carbon Tetrachloride
B.p./760 mm Hg (°C) . .	56·06	80·01	76·65
$d_4^{25\cdot00}$	0·78424	0·87371	1·58452
$n_D^{25\cdot00}$	1·35598	1·49796	1·45736
Vapour pressure 45·00 °C	512·72	223·66	258·84

of 75 : 1, in the column described by Brown and Ewald (1951), rejecting a small head and a large tail fraction. The density of the product was d_4^{25} 0·78424 which agrees with that obtained by Thirion and Craven (1952). Timmermans (1950) reports the values d_4^{25} 0·78501 and n_D^{25} 1·35662, both considerably higher than our values shown in Table 1. According to Glazunov (1914), a high

TABLE 2

VAPOUR PRESSURE OF ACETONE

t (°C)	P (mm Hg)	Antoine Equation Constants
37·68	388·19	$A=7\cdot19958$
41·58	450·99	$B=1254\cdot51$
44·96	512·08	$C=234\cdot42$
45·00	512·80	$\sigma=0\cdot11$ mm Hg
45·00	512·85	
47·01	552·07	
49·31	599·82	
51·91	658·01	
56·02	759·06	
56·06	760·00	
56·07	760·26	
56·08	760·33	

refractive index is indicative of the presence of water. Therefore, it appears that careful fractional distillation in an efficient column is the safest method for drying acetone. Chemical methods have the weakness that water may be formed from acetone condensation reactions at a faster rate than it is removed by the dehydrating agent. These findings are in agreement with those of Riddick (1955).

The physical properties of the liquids used are shown in Table 1. The vapour pressures of the benzene and carbon tetrachloride samples were checked at 45 °C and at the normal boiling point, using the equilibrium still, and found to be in good agreement with values previously obtained by us. The vapour pressures of acetone were measured over a range of temperatures and are given in Table 2. These values were fitted by the method of Willingham *et al.* (1945) to the Antoine equation

$$\log_{10} P = A - \frac{B}{C+t},$$

where P is in standard mm Hg and t in °C. The values of the constants found and σ, the standard deviation of the fit, are given in Table 2.

(*c*) *Analytical Methods*

A number of mixtures was prepared from weighed amounts of the components ; their compositions and refractive indices are given in Tables 3 and 4.

TABLE 3

ACETONE + BENZENE

Refractive index : composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0475	1·49222	0·4988	1·43308
0·0916	1·48680	0·6091	1·41723
0·1946	1·47394	0·6921	1·40485
0·3002	1·46018	0·7973	1·38870
0·3851	1·44887	0·8994	1·37248
0·4969	1·43337	0·9633	1·36207

TABLE 4

ACETONE + CARBON TETRACHLORIDE

Refractive index : composition data

x_1	$n_D^{25\cdot00}$	x_1	$n_D^{25\cdot00}$
0·0565	1·45285	0·4850	1·41555
0·0785	1·45111	0·4992	1·41422
0·2075	1·44061	0·5965	1·40428
0·3023	1·43244	0·7089	1·39208
0·3365	1·43171	0·7869	1·38308
0·3813	1·42533	0·8904	1·37036
0·4085	1·42284	0·9393	1·36412

The method of Brown and Smith (1954) was employed to calculate the compositions of the liquid and vapour samples from the refractive index measurements.

III. Results

The liquid-vapour equilibrium data are presented in Tables 5 and 6 where x and y are the mole fractions of acetone in the liquid and the vapour respectively, P is the total pressure in standard mm Hg, and α is the relative volatility given by $\alpha = y_1 x_2 / y_2 x_1$.

Table 5

Acetone + benzene 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0470	0·1444	250·73	3·422	277·6	3·1	16·0
0·0963	0·2574	275·02	3·253	244·4	4·9	28·0
0·2207	0·4417	324·25	2·794	162·0	21·3	52·4
0·2936	0·5204	348·40	2·611	131·0	32·6	61·5
0·4011	0·6139	379·88	2·374	88·3	54·6	68·1
0·4759	0·6697	399·73	2·233	66·0	72·6	69·5
0·6125	0·7614	432·95	2·019	35·8	108·9	64·1
0·7045	0·8201	453·99	1·912	22·7	132·2	55·1
0·8081	0·8805	475·39	1·750	8·8	176·6	41·0
0·9084	0·9418	495·32	1·632	2·1	216·1	21·7
0·9529	0·9699	503·96	1·593	0·8	231·8	11·7

Table 6

Acetone + carbon tetrachloride 45·00 °C

Experimental data and derived functions

x_1	y_1	P	α	μ_1^E	μ_2^E	G_x^E
0·0556	0·2165	315·32	4·694	567·9	4·7	36·0
0·0903	0·2910	339·70	4·135	493·5	11·6	55·1
0·2152	0·4495	397·77	2·976	314·7	44·0	102·2
0·2929	0·5137	422·46	2·550	240·3	68·9	119·1
0·3970	0·5832	448·88	2·125	164·6	110·4	131·9
0·4769	0·6309	463·92	1·875	118·0	144·4	131·8
0·5300	0·6621	472·84	1·738	93·0	168·6	128·5
0·6047	0·7081	485·16	1·586	67·4	202·1	120·6
0·7128	0·7718	498·07	1·363	33·4	265·7	100·1
0·8088	0·8360	506·89	1·205	14·4	326·4	74·0
0·9090	0·9141	512·32	1·065	3·1	395·4	38·8
0·9636	0·9636	513·20	1·000	0·6	435·5	16·4

From graphs of the data shown in Table 6, it was concluded that the system acetone + carbon tetrachloride forms an azeotrope at 45·00 °C at a mole fraction of acetone of 0·964 and a pressure of 513·2 mm Hg.

IV. Derived Thermodynamic Functions

The excess chemical potentials μ_1^E and μ_2^E and the excess free energy G_x^E were calculated from the equilibrium data using equations (**2**), (**3**), and (**4**) of Brown and Smith (1954). The values obtained (cal/g-mol) are shown in Tables

5 and 6. For these calculations it is necessary to know the liquid molar volumes and the second virial coefficients of the vapours for each component. Liquid molar volumes V_1 and V_2 were obtained from densities given by Timmermans (1950); the value of the second virial coefficient for acetone was obtained from the data of Lambert (1949), that for benzene from equation (A5) of Allen, Everett, and Penney (1952), and the value for carbon tetrachloride was calculated from critical data using the Berthelot equation. The second virial coefficients (β_{12}) in the equation of state for the mixed vapours and the allied coefficients (δ_{12}) were calculated by the method given by Brown and Smith (1954). For the system acetone+benzene at 45·00 °C, the second virial coefficients and molar volumes (l/mol) were taken to be

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−1·66	−1·23	−1·03	+0·84	0·08	0·09

For acetone+carbon tetrachloride at 45·00 °C the values used were

β_{11}	β_{22}	β_{12}	δ_{12}	V_1	V_2
−1·66	−1·24	−1·05	+0·80	0·08	0·10

V. Discussion

The excess free energy data were fitted by the method of least squares to equation (1)

$$G_x^E = x_1x_2[a+b(x_1-x_2)+c(x_1-x_2)^2]. \quad \ldots\ldots\ldots\ldots \quad (1)$$

For the system acetone+benzene at 45 °C the values of the constants (cal/g-mol) and the standard deviation of the fit (σ) were

a	b	c	σ
280·3	−37·3	0	1·0

These values do not indicate separation into two liquid phases. The thermodynamic consistency of the results was tested by the method used previously (Brown and Smith 1954), the ratio of areas above and below datum on a plot of $\mu_1^E-\mu_2^E$ against x, was 1·05. Errors in G_x^E due to errors in the directly measured quantities were estimated to be $\pm 2\cdot 0$ cal/mol. For comparison, values of G_x^E were calculated from the data of Litvinov (1940) at 25 and 35 °C, but they are higher than the values reported here and show too great a change with temperature.

For acetone+carbon tetrachloride at 45·00 °C the constants obtained by fitting the excess free energy data to equation (1) were

a	b	c	σ
523·1	−111·5	+65·3	0·6

In the test for thermodynamic consistency the ratio of the two areas was 1·005, and the errors in G_x^E due to those in the measured quantities were estimated to be ± 4 cal/mol.

The values of G_x^E calculated from the results of Severns *et al.* (1955) at 50 °C are in reasonable agreement with our data for 45 °C. Values of G_x^E at 45 °C were also calculated from the three sets of isobaric data of Bachman and Simmons (1952), but the values obtained were 10 per cent. higher than those given here.

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CHEMISTRY OF POLYNUCLEAR COMPOUNDS

I. THE INFRA-RED SPECTRA OF SOME POLYNUCLEAR QUINONES AND POLYNUCLEAR AROMATIC HYDROCARBONS

By R. A. Durie,* Ruth E. Lack,* and J. S. Shannon*

[*Manuscript received July* 10, 1957]

Summary

In an investigation into the coking mechanism of coal, polynuclear quinones were adopted as models. The infra-red absorption spectra (between 2000 and 650 cm^{-1}) are now reported for several of these quinones, namely: dibenzanthrone (I); *iso*dibenzanthrone (II); 16,17-dimethoxydibenzanthrone (III); 16,17-diethoxydibenzanthrone (IV); pyranthrone (V); flavanthrone (VI); 4,10-dibromoanthanthrone (VII); 4,4′-dibenzanthronyl (VIII); 2,2′-dimethyl 1,1′-dianthraquinoyl (IX); and for the polynuclear aromatic hydrocarbons violanthrene (X) and *iso*violanthrene (XI). Factors influencing the quinonoid carbonyl group bond order (hence frequency of absorption) and the redox potential are discussed. Tentative correlations are advanced for strong absorption bands in the CH out-of-plane vibration region. The carbonyl group frequencies and the electronic absorption spectra indicate the molecular non-planarity of VIII and IX.

I. Introduction

As part of a programme aimed at elucidating the chemical reactions that occur during the coking of coal, the study of the pyrolytic reactions and coking of a series of polynuclear quinones has been undertaken. In this work, details of which will be reported later in the present series of papers, the infra-red spectra of the quinones and the hydrocarbons, violanthrene and *iso*violanthrene, have been examined. The spectra of the quinones are of additional interest since it has been suggested by Brown (1955) that the strong band occurring near 1600 cm^{-1} in all coal spectra is due, at least in part, to the presence of hydrogen-bonded quinonoid carbonyl groups.

Although there is a fairly extensive literature concerned with the correlation of the quinone carbonyl group stretching frequency with molecular structure, some confusion still surrounds this subject. Further, there has been little published discussion on other regions of the spectra of even the simplest quinones. Systematic comparison of the infra-red spectra presented in this paper is difficult, owing to the wide structural differences of the quinones, which were not primarily chosen for infra-red study. However, some effort has been made to discuss features of the spectra between 2000 and 650 cm^{-1} rather than limit the study to the carbonyl frequencies.

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II. Experimental

The quinones studied were carefully purified by conventional recrystallization and sublimation procedures. The hydrocarbons violanthrene and *iso*violanthrene were isolated from the pyrolytic products of dibenzanthrone and *iso*dibenzanthrone respectively and purified by sublimation. The spectra of all compounds

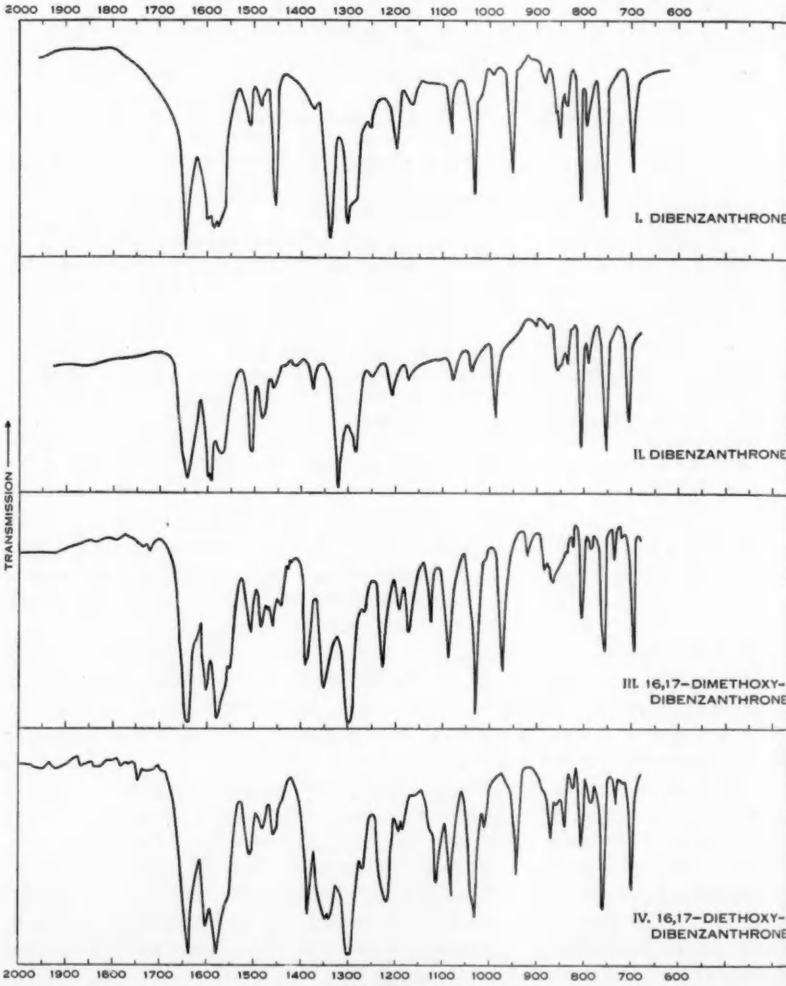


Fig. 1.—Infra-red spectra of dibenzanthrone (I), *iso*dibenzanthrone (II), 16,17-dimethoxydibenzanthrone (III), and 16,17-diethoxydibenzanthrone (IV).

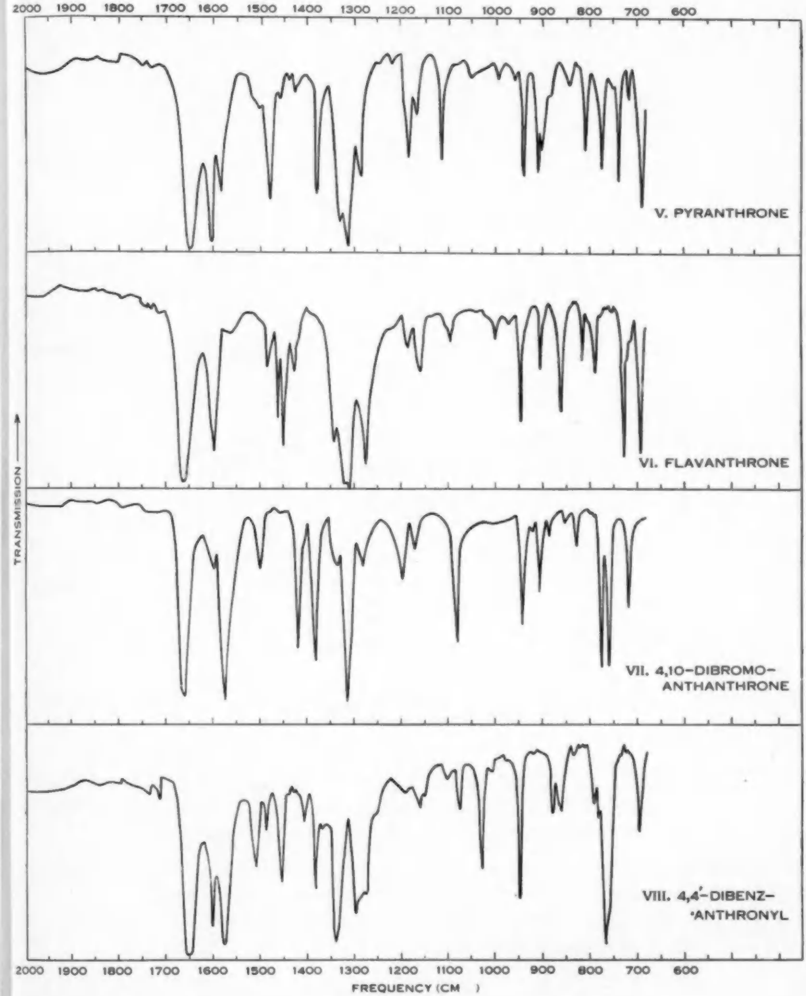


Fig. 1 (*Continued*).—Infra-red spectra of pyranthrone (V), flavanthrone (VI), 4,10-dibromoanthanthrone (VII), and 4,4'-dibenzanthronyl (VIII).

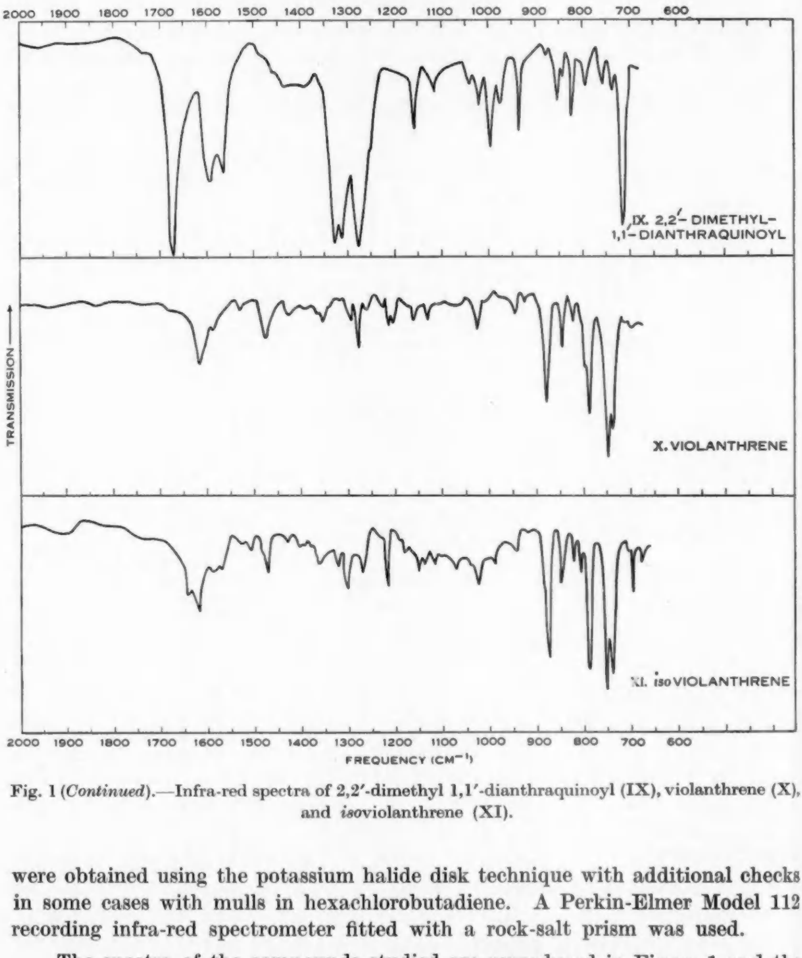


Fig. 1 (*Continued*).—Infra-red spectra of 2,2′-dimethyl 1,1′-dianthraquinoyl (IX), violanthrene (X), and *iso*violanthrene (XI).

were obtained using the potassium halide disk technique with additional checks in some cases with mulls in hexachlorobutadiene. A Perkin-Elmer Model 112 recording infra-red spectrometer fitted with a rock-salt prism was used.

The spectra of the compounds studied are reproduced in Figure 1 and the salient features are summarized in Table 1. The measured wave numbers were reproducible to within ± 1 cm^{-1} below 1300 cm^{-1} and to within ± 2 cm^{-1} at 1700 cm^{-1} when the bands were sharp.

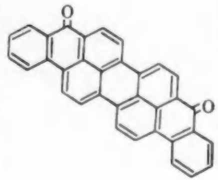
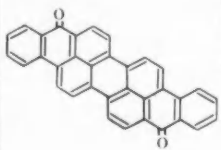
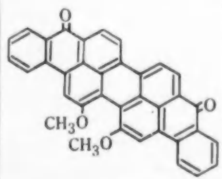
III. Discussion

In the following discussion the spectra of the regions 1700–1500, 1500–900, and 900–650 cm^{-1} are considered separately.

The spectra of the two polynuclear hydrocarbons show strong absorption bands near 1600 and below 900 cm^{-1} and numerous weaker bands between 1600

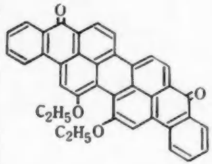
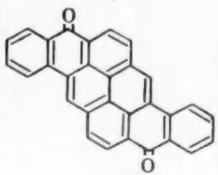
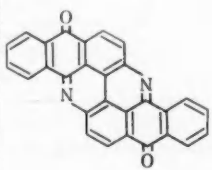
TABLE 1

PRINCIPAL INFRA-RED ABSORPTION BANDS

Compound	Structural Formula	Principal Absorption Bands (cm^{-1})*				
		2000–1500	1500–1300	1300–1100	1100–900	900–650
A. Polynuclear Quinones I. Dibenzanthrone (Violanthrone)		1645VS 1599S 1587S 1575VS 1509WM	1482W 1383W 1455S 1336VS 1302VS	1284Sh 1196MS 1250W 1160W	1082M 950S 1032S	881W 792WM 696S 859W 753S 848WM 837W 806S
II. *iso*Dibenzanthrone (*iso*Violanthrone)		1644S 1587S 1600S 1569S 1508S	1478M 1382WM 1459W 1322VS	1285S 1172W 1250W 1208M	1074WM 988S 1038WM	858M 849M 790WM 834M 754S 811WSh 705S 805S
III. 16,17-Dimethoxydibenzanthrone		1640VS 1597S 1578VS 1552Sh 1508MS	1483WM 1387S 1459M 1355S 1438WM 1300VS	1268W 1190WM 1245W 1170MS 1228S 1124MS	1088S 971S 920W 1030S	882W 786W 693S 865MS 754S 834W 733M 823W 802S

* W, weak ; WM, weak to medium ; M, medium ; MS, medium to strong ; S, strong ; VS, very strong ; Sh, shoulder.

TABLE 1 (*Continued*)

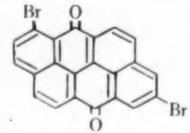
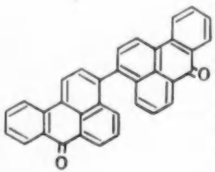
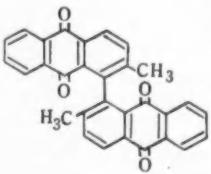
Compound	Structural Formula	Principal Absorption Bands (cm^{-1})* 2000–1500	1500–1300	1300–1100	1100–900	900–650
IV. 16,17-Diethoxy-dibenz-anthrone		1639VS 1578VS 1555Sh 1601S 1509M	1483M 1386S 1457M 1348S 1340S	1299VS 1191WM 1290VS 1182WM 1268M 1127Sh 1218S 1111S	1078S 942S 1038Sh 1030S 1010WM	887W 782WM 699S 870M 758S 840M 731WM 822WM 804S
V. Pyranthrone		1642VS 1579M 1600S	1497W 1375S 1475S 1453W 1325S 1433W 1309VS 1420W	1285MS 1180S 1214W 1164M 1110S	1046W 989W 954W 935S 905S	896S 768S 686S 878Sh 734S 838WM 713WM 804S
VI. Flavanthrone		1655VS 1596S	1480M 1369M 1448S 1422S 1339S 1316VS 1306VS	1271S 1181WM 1156M 1102WSh	1093WM 995W 968VW 944S 902MS	855S 785MS 690S 813M 725S

* W, weak ; WM, weak to medium ; M, medium ; MS, medium to strong ; S, strong ; VS, very strong ; Sh, shoulder.

TABLE 1 (*Continued*)

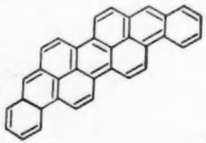
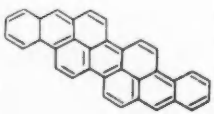
* W, weak ; WM, weak to medium ; M, medium ; MS, medium to strong ; S, strong ; VS, very strong ; Sh, shoulder.

Table 1 (*Continued*)

Compound	Structural Formula	Principal Absorption Bands (cm^{-1})*				
		2000–1500	1500–1300	1300–1100	1100–900	900–650
VII. 4,10 - Dibromo-anthanthrone		1657VS 1597WM 1573VS	1498M 1380S 1415S 1341W 1313S 1301W	1278M 1197M 1168M	1080S 941S 1067W 904MS	882WM 772S 852W 757S 825WM 715MS
VIII. 4 , 4′ - Dibenz-anthronyl		1650VS 1577VS 1601S 1509S	1484M 1380MS 1456S 1339VS 1405M 1321Sh	1295S 1191W 1275S 1160WM 1258S 1150W 1103W	1075M 950S 1029S	878M 791WM 696S 867M 777WM 861M 764VS 835W 759Sh
IX. 2, 2′ - Dimethyl-1,1′-dianthra-quinoyl		1672VS 1594S 1564S	1328VS 1313VS	1276VS 1159MS 1252Sh 1116W	1039W 995MS 1022WM 973WM 934MS	852MS 794WM 841W 756WM 822MS 738WM 713VS

* W, weak ; WM, weak to medium ; M, medium ; MS, medium to strong ; S, strong ; VS, very strong ; Sh, shoulder.

TABLE 1 (*Continued*)

Compound	Structural Formula	Principal Absorption Bands (cm⁻¹)*										
		2000–1500		1500–1300		1300–1100		1100–900		900–650		
B. Polynuclear Hydrocarbons												
X. Violanthrene		1616S	1587W	1474M	1366W	1294W	1160W	1024W	945W	877S	796MSh	
			1530W	1427WM	1355WM	1278M	1130W	1008VW	926W	845M	789S	
					1340W	1260W				824WM	748S	
					1317W	1234W				806W	738S	
						1208WM						
						1203WM						
XI. *iso*Violanthrene		1642WM	1583M	1469M	1380W	1270WM	1182W	1074W	988W	886Sh	791S	697M
		1617S	1573W	1430W	1362W	1214MS	1149W	1021WM	943W	875S	787S	679W
			1529W	1402W	1321W		1138W			844M	751S	
			1508W		1320W		1114W			823WM	739S	
					1301M					807WM		

* W, weak; WM, weak to medium; M, medium; MS, medium to strong; S, strong; VS, very strong; Sh, shoulder.

and 900 cm^{-1}. The spectra of the polynuclear quinones are rich in strong bands between 1700 and 700 cm^{-1}, with consistently prominent features near 1600 and 1300 cm^{-1}, and in the region below 900 cm^{-1}.

(a) *The Region 1700–1500 cm^{-1}*

Absorption bands in the region 1700–1500 cm^{-1} are normally due to the stretching vibrations of unsaturated bonds between atoms. As regards the polynuclear quinones reported here, the intense high-frequency band (near 1650 cm^{-1}) which is always present in the spectra of all these compounds has been identified as the quinonoid C=O group frequency (cf. Josien and Fuson 1952); strong bands occurring between 1470 and 1600 cm^{-1} probably arise from aromatic ring C=C bond vibrations. These absorption bands are discussed in more detail below.

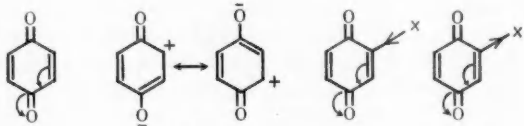
(i) *1600–1470 cm^{-1}*.—The polynuclear aromatic hydrocarbons violanthrene and *iso*violanthrene are each characterized in this region by a single strong absorption band near 1615 cm^{-1} (with a weaker band near 1475 cm^{-1}), which is weaker but somewhat broader than the strong absorption bands which occur below 900 cm^{-1}. This is at variance with Cannon and Sutherland's (1951) generalization that when there are four or more condensed rings, absorption at 1500 and 1600 cm^{-1} is very weak.

The polynuclear quinones consistently show one or more intense absorption bands between 1600 and 1470 cm^{-1} with the strongest band or bands lying closer to 1600–1550 cm^{-1}. The relatively more intense absorption in this region in the dibenzanthrone series I-IV when compared with the parent hydrocarbons strongly suggests that the quinonoid carbonyl group is in some way responsible. The effect may be analogous to the enhancement of the 1580 cm^{-1} band in simple aromatic compounds through external conjugation with the ring, as in the benzoyl group (Bellamy 1954, pp. 59–63).

(ii) *C=O Group Frequency in Quinones (1700–1600 cm^{-1})*.— Four factors are known to influence the quinonoid C=O group frequency. Conjugation and/or hydrogen bonding with the C=O group or electropositive substituents cause a decrease in frequency, whereas steric strain or electronegative substituents raise the frequency above its " normal " value. These influences must act in a manner to bring about a change in strength, that is, bond order, of the carbon-oxygen linkage. Josien and Fuson (1952) and Josien *et al.* (1953) have made an extensive study of the C=O frequency in a wide range of polynuclear quinones with a view to obtaining useful correlations between this frequency and such factors as the redox potential, the number of fused rings, and the index of free valence on the parent hydrocarbon. These parameters are essentially different manifestations of those electronic influences which lead to a variation in the C=O bond order. Indeed, these authors have also shown that the quinonoid carbonyl frequency is to a first approximation a function of the calculated bond order. Similarly, Tanaka, Nagakura, and Kobogashi (1956) have obtained a correlation between carbonyl group frequency and C=O bond order in substituted acetophenones and benzoic acids.

Although no direct comparison of the results reported in the present paper is made with redox potentials, this opportunity is taken to comment on those factors influencing the redox potential and the carbonyl group frequency.

A rigid correlation between carbonyl group frequency and redox potential of a quinone is not to be expected on theoretical grounds. As stated earlier, the carbonyl group frequency will vary with the bond order of the carbon-oxygen linkage but as shown below the redox potential is not necessarily determined by the C=O bond order. The effect of substituents on the carbonyl frequency and redox potential may be explained on the basis of the influence these substituents have on the canonical forms contributing to the resonance hybrid of the quinone. With the simplest quinone (1) the principal charged structures contributing to the quinone resonance hybrid may be represented by the form (2).



(1) (2) (3) (4)

When an electron-donating substituent is present the mesomeric shift as indicated in (3) is facilitated and structures of the type (2) will contribute more to the resonance hybrid of (3) than of (1). Thus the carbon-oxygen bond is weaker, and the frequency lower, in (3) than in (1). Conversely, an electron-attracting substituent will inhibit the mesomeric shift indicated in (4) and structures of the type (2) will contribute less to the resonance hybrid of (4) than of (1). Therefore, the carbon-oxygen bond is stronger and the frequency higher in (4) than in (1). Furthermore, since the redox potential will increase with the strength of the quinonoid C=C bonds of the quinones (cf. Badger 1954) the facilitated mesomeric shift indicated in (3) will lower the C=C bond order and therefore lower the redox potential of (3) compared with (1). Similarly, the electron-attracting substituent in (4) will strengthen the C=C bond and increase the redox potential. Peters and Sumner (1953) have suggested that inhibited electronic shifts as in (4) and facilitated shifts as in (3) respectively account for the small shifts in the ultraviolet spectra of anthraquinones substituted with electron-attracting groups and for the much larger shifts in the spectra of anthraquinones with electron-donating substituents.

In non-extended condensed polynuclear quinones the ethylenic character of the quinonoid carbon-carbon bonds is modified by the participation of these bonds in aromatic-type resonance with the hydrocarbon moieties of the molecules and, as stated above, the redox potential will vary inversely with the quinonoid carbon-carbon bond orders. Further, the more these quinonoid carbon-carbon bonds participate in resonance with the other condensed rings the less these are able to conjugate with the quinonoid carbonyl group, and thus the carbon-oxygen bond order and frequency will increase (Sidman 1956); Josien and Deschamps

(1955) have recently attempted to verify this relationship by theoretical calculation. This effect can best be illustrated by reference to Table 2.

Table 2 lists the sum of the two quinonoid carbon-carbon bond orders. The values given were derived by using the results of Coulson *et al.* (cf. Badger 1954) for the bond orders of aromatic hydrocarbons. For example, the carbon-carbon bond in benzoquinone (1) was, as an approximation, assigned the order 2, which is Coulson's figure for ethylene. Therefore, the total bond order for benzoquinone as given in Table 2 is $2+2$ ($=4$). Similarly for naphthoquinone (3) the figure 3·667 is made up of 2 (the isolated "ethylene" bond) plus 1·667 (the bond order of a benzene carbon-carbon bond). For naphthacenequinone (9) the figure 3·270 is derived from 1·667, the benzene carbon-carbon bond order, and 1·603, the 3,4-carbon-carbon bond order of naphthalene. The values for the other quinones were similarly obtained. These bond orders do not allow for the effect of conjugation between the aromatic moieties on either side of the ring containing the carbonyl groups, nor between the quinonoid C=O and C=C bonds and are therefore probably too high. However, a more precise value for these bond orders is difficult to obtain. For benzoquinone a quinonoid C=C bond length of 1·32 Å has been reported (Robertson 1935), which is less than the accepted value of 1·35 Å (Wheland 1955) for a true ethylenic double bond, and thus the normal empirical bond order/bond length relationships predict a bond order greater than 2. However, since the carbonyl frequency of benzoquinone is about 50 cm^{-1} lower than the "normal" unconjugated carbonyl frequency there must be significant conjugation between the quinonoid C=O and C=C bonds (cf. form (2) on p. 438). The effect of this conjugation with the quinonoid C=O bonds on the quinonoid C=C bond order will be a maximum in the case of benzoquinone. Even if it is assumed that this effect results in a proportionate contribution to the quinonoid C=C bond order throughout the series listed in Table 2, this bond order will have to be as low as 1·6 for benzoquinone before the sequence of the bond order in Table 2 is upset.

Now, as disclosed in Table 2, for linearly condensed quinones [1, 3, (4), 8, 9, (10)]* the values do agree with the concept that carbonyl frequency increases with carbon-oxygen bond order; but the magnitude of the successive increases in the bond order and frequency progressively diminishes as the number of linearly-condensed rings increases. Also the redox potential can be seen to vary inversely as the total quinonoid carbon-carbon bond order for both the linear and angular quinones.

The variation of the carbonyl frequency is more complex in the angular quinones. For the angular *p*-quinones 5, 6, and 7 (Table 2), the carbonyl frequencies change in an irregular manner with the total carbon-carbon bond order. It is felt that a systematic study of a wider series of angular quinones must be made before a satisfactory explanation can be found for this anomalous behaviour. Since the redox potentials vary in the expected manner with change in the total quinonoid carbon-carbon bond order (and hence carbon-oxygen

* The numbers in brackets refer to those quinones for which no values of the carbonyl frequencies are available (see Table 2).

TABLE 2

CARBON-CARBON BOND ORDERS OF QUINONES

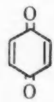
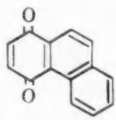
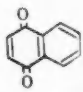
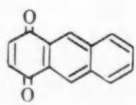
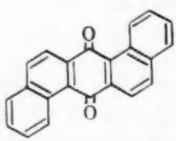
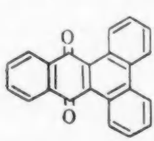
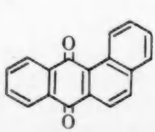
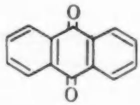
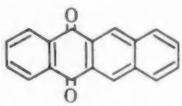
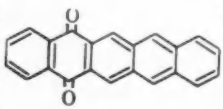
Compound	Structural Formula	M.p. (°C)	Redox Potential (V)	Total C=C Bond Order	Carb. Freq. (cm^{-1})	
					(*a*)‡	(*b*)§
1. Benzoquinone		115·7	0·71*	4·000	1667	1665
2. 1,4-Phenanthraquinone		155	0·53†	3·725		
3. 1,4-Naphthoquinone		125–126	0·49*	3·667	1675	1662
4. 1,4-Anthraquinone		218 (*d*)	0·40†	3·603		
5. 1,2,5,6-Dibenzanthraquinone		245	0·27†	3·450	1660	1652
6. 1,2,3,4-Dibenzanthraquinone		181–183		3·442	1668	1662
7. 1,2-Benzanthraquinone		169	0·23†	3·392	1670	1664

TABLE 2 (*Continued*)

Compound	Structural Formula	M.p. (°C)	Redox Potential (V)	Total C=C Bond Order	Carb. Freq. (cm^{-1})	
					(*a*)‡	(*b*)§
8. Anthraquinone		286	0·16*	3·334	1678	1671
9. Naphthacene-quinone		294	—0·31*	3·270	1682	
10. Pentacene-quinone			—0·98*	3·253		

* Clar (1952).
† Branch and Calvin (1941).
‡ Solution (Josien *et al.* 1953).
§ Solid (Josien and Fuson 1952).

bond order) it seems that intermolecular rather than intramolecular forces may be responsible. However, these intermolecular forces would have to persist in solution to explain satisfactorily the parallel behaviour in solid and solution (Table 2). In this respect it may be significant that there is a systematic increase in melting point and carbonyl frequency for linear quinones, whereas both vary in an irregular manner for angular quinones (Table 2).

With extended quinones, such as those described in the present paper, the above conjugation and configurational effects become much more complex.

(*b*) *Carbonyl Group Frequencies of Compounds I–IX*

The carbonyl frequencies of dibenzanthrone (I), *iso*dibenzanthrone (II), and pyranthrone (V) have been found to be 1645, 1644, and 1642 cm^{-1} respectively. These values are very close to results (1645, 1646, 1646 cm^{-1}) published by Josien and Fuson (1952), but differ from those (1638, 1655 cm^{-1}) for I and V of Hadzi and Sheppard (1951). The similarity of the frequencies of the three quinones may be due to the comparable lengths of the shortest conjugated chain between the respective oxygen atoms, namely, 10 conjugated carbon atoms in I and V and 12 in II.

16,17-Dimethoxydibenzanthrone (III), 16,17-diethoxydibenzanthrone (IV), and 4,10-dibromoanthanthrone (VII) have carbonyl frequencies at 1640, 1639,

and 1657 cm^{-1} respectively which illustrate the effect of substituents. For example, by virtue of their electron-donating powers, the diethoxy and dimethoxy groups lower the frequencies of diethoxydibenzanthrone and dimethoxydibenzanthrone with respect to the parent dibenzanthrone by 6 and 5 cm^{-1} respectively. Conversely, the electron-attracting powers of bromine groups increase the carbonyl frequency of anthanthrone from 1650 (Josien and Fuson 1952) to 1657 cm^{-1} (Josien and Fuson report 1655 cm^{-1}).

Flavanthrone (VI) offers another example of the effect of electron attraction away from the carbonyl groups. Nitrogen is more electronegative than carbon and in flavanthrone tends to attract more electrons than the corresponding carbon atoms do in pyranthrone; this readily explains why the carbonyl frequency of flavanthrone is 13 cm^{-1} higher than that of pyranthrone.

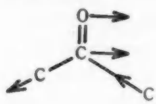
Padhye, Rao, and Venkataraman (1953) have shown that the electronic absorption spectra of benzanthrone and 4,4′-dibenzanthronyl (VIII) are very similar and have therefore concluded that owing to steric hindrance there is no possibility of extended conjugation across the C—C bond connecting the two benzanthronyl residues of 4,4′-dibenzanthronyl. Therefore, it would follow that the carbonyl frequencies of benzanthrone and 4,4′-dibenzanthronyl should be very similar, and this has been confirmed. The carbonyl frequency of 4,4′-dibenzanthronyl is 1650 cm^{-1} while Josien and Fuson (1952) have reported that for benzanthrone to be 1649 cm^{-1}.

Another interesting example in which steric hindrance inhibits free conjugation is given by 2,2′-dimethyl 1,1′-dianthraquinoyl (IX). If hindrance between the methyl groups and the quinonoid oxygen atoms prevents coplanarity of the molecule, the electronic absorption spectrum of the molecule should be very close to that of 2-methylanthraquinone. This is in fact the case, since 2,2′-dimethyl 1,1′-dianthraquinoyl in dioxane solution has $\lambda_{max.}$ 255 mμ, log ε 4·8; 332 mμ, log ε 4·0 (Lack and Shannon, unpublished data) and anthraquinone in dioxane solution has $\lambda_{max.}$ 252 mμ, log ε 4·6; 322 mμ, log ε 3·6 (Friedel and Orchin 1951). The small differences observed can be attributed to the bathochromic shift due to the methyl groups in the former. Confirmatory evidence for this lack of conjugation between the anthraquinone moieties is supplied by a study of the respective carbonyl frequencies. The present results disclose that 2,2′-dimethyl 1,1′-dianthraquinoyl absorbs at 1672 cm^{-1} while 2-methylanthraquinone absorbs at almost the same frequency of 1676 cm^{-1} (Flett 1948).

(c) *The Region 1500–900 cm^{-1}*

The infra-red spectra of the polynuclear quinones in the region 1500–900 cm^{-1} are rich in strong bands. These will consist largely of skeletal vibrations, about which little comment can be made. However, one feature that appears consistently throughout all these spectra is a very intense region of absorption near 1300 cm^{-1} (1350–1275 cm^{-1}). Hadzi and Sheppard (1951) have also observed in several polynuclear quinones strong absorption in the region 1350–1200 cm^{-1} which they have suggested may be due to some motion of the carbonyl group coupled with the rest of the molecule. Simple aryl and alkyl ketones absorb

strongly near 1300 cm^{-1} (1225–1075 and 1325–1215 cm^{-1} respectively; Bellamy 1954, p. 133) and Francis (1951) has gone further to suggest that this arises from a deformation vibration of the type



There is no doubt that this frequency is connected with the carbonyl group, and the narrow region in which it occurs for a wide range of quinones indicates that coupling of this vibration with those of the rest of the molecule must be slight.

(*d*) *The Region 900–650 cm^{-1}*

All the polynuclear quinones, as well as the two hydrocarbons studied, have one or more strong absorption bands in the region between 900 and 650 cm^{-1}. The strong bands which occur in this region in benzene derivatives are known to be associated with the out-of-plane bending vibrations of the aromatic ring CH groups (Bellamy 1954, p. 64).

Cannon and Sutherland (1951) have also shown that polynuclear aromatic hydrocarbons generally possess a number of sharp bands here which they have associated with the CH out-of-plane bending vibrations.

The position and number of bands in the 900 to 650 cm^{-1} region is very characteristic of particular substitution types for the simple benzene derivatives (Bellamy 1954, p. 64). Cannon and Sutherland (1951) studied in detail the absorption patterns in this region for a wide range of condensed polynuclear aromatic hydrocarbons and were unable to find any obvious correlations with the configuration of the aromatic rings in the molecule. These authors tentatively suggested that for condensed ring systems containing three or more rings, bands near 750 cm^{-1} arise from C—H bonds that are approximately parallel to the longer axis of the molecules, and bands near 900 cm^{-1} arise from C—H bonds approximately perpendicular to the long axis of the molecule; also that bands near 810 cm^{-1} are associated with angular condensation. Dannenberg, Schiedt, and Steidle (1953) have analysed in some detail the low-frequency bands of a series of substituted *cyclo*pentenophenanthrenes and have classified these bands in terms of the distribution of the residual hydrogen atoms in the aromatic ring system. Fuson and Josien (1956) have successfully extended this approach to the methyl 1,2-benzanthracenes with favourable agreement with the generalized conclusions of Dannenberg, Shiedt, and Steidle (1953). To facilitate reference to this earlier work when discussing the spectra described in the present paper the above assignments are summarized in Table 3.

Although several studies have been reported of environmental influences on the quinone carbonyl frequency in simple quinones and polynuclear quinones, the complete infra-red spectra of this class of compound do not appear to have been studied in detail. Yates, Ardaó, and Fieser (1956) have reported the complete spectra over the region 2000 to 650 cm^{-1} for a series of substituted

p-benzoquinones. These authors suggest that a strong band in the range 917 to 877 cm^{-1} is associated with the presence of isolated hydrogen atoms on the ring and that a medium-strong band between 840 and 806 cm^{-1} appears to be associated with two adjacent hydrogen atoms on the ring. Cannon and Sutherland (1951) have published the spectrum of dibenzanthrone (I) and Wyman (1956) has tabulated the characteristic bands of indanthrone without comment.

The present researches have disclosed that the dibenzanthrone series—dibenzanthrone (I), *iso*dibenzanthrone (II), 16,17-dimethoxydibenzanthrone (III), and 16,17-diethoxydibenzanthrone (IV)—have a remarkably similar absorption pattern in the 900–650 cm^{-1} region with strong bands between 705 and 693 cm^{-1} (696, 705, 693, and 699 cm^{-1} respectively), between 758 and 753 cm^{-1} (753, 754, 754, and 758 cm^{-1} respectively), and between 806 and 802 cm^{-1} (806, 805, 802, and 804 cm^{-1} respectively). Analyses of the structures of this series of quinones in terms of number of adjacent C—H groups on each peripheral

TABLE 3

CHARACTERISTIC AROMATIC CH OUT-OF-PLANE FREQUENCY RANGES

Number of Adjacent Hydrogen Atoms on a Ring	1	2	3	4	5
Compound type:					
Substituted benzenes ..	900–860	860–800	810–750	770–735	730–700 710–690
Substituted *cyclo*penteno-phenanthrenes		873–810	757–754 792–786	762–741	
Substituted benzanthracenes	900–870	830–790	792–786	746–738	

ring reveal that all contain two or more rings with two adjacent CH groups and two rings with four adjacent CH groups. In addition, III and IV each have two rings containing lone CH groups. Also all four contain three rings with no CH group whatever. Comparison of the strong absorption bands for I-IV in this region with the summarized correlations in Table 3, suggests that the absorption at 806–802 cm^{-1} is associated with the out-of-plane bending vibration of two adjacent CH groups (i.e. 1,2,3,4-tetra-substitution due to condensation) whereas the strong absorption between 758 and 753 cm^{-1} is characteristic of the presence of four adjacent CH groups on a ring (i.e. *ortho*-substitution due to condensation). Further confirmation of the validity of assigning these vibrations to the CH out-of-plane bending vibration is obtained by considering the relative intensities of the bands (see Table 1 and Fig. 1). Structures I and II, despite the different condensed ring configuration, have identical adjacent CH group patterns (three rings with no CH group, four rings with two groups adjacent, and two rings with four adjacent groups) and the relative intensities of the bands near 805, 754, and 700 cm^{-1} are very similar for both compounds (i.e. unaffected by change in ring configuration). Furthermore, with III and IV, which only have two rings with adjacent pairs of CH groups, the band near 803 cm^{-1} is noticeably much

weaker relative to the band near 755 cm^{-1}, the latter being due to four adjacent CH groups which are present to the same extent in III and IV as in I and II. In addition, III and IV have each two isolated CH groups, but no absorption can be assigned unambiguously to this type of group in the region 900–860 cm^{-1} (cf. Table 3). Not only I and II (containing no isolated CH groups) but also III and IV show broad absorption in this region.

The medium-strong intensity band occurring between 705 cm^{-1} for I, III, and IV, and 693 cm^{-1} for II, cannot be correlated with the CH out-of-plane vibrations and is possibly a skeletal ring vibration (cf. 683–681 cm^{-1} in methyl 1,2-benzanthracenes reported by Fuson and Josien 1956).

The hydrocarbons violanthrene and *iso*violanthrene are also remarkably similar in the region 900–650 cm^{-1}. The absorption spectra of both show a strong partially resolved doublet at 748–738 and 751–739 cm^{-1} respectively and a strong band at 877 and 875 cm^{-1} respectively. Only the appearance of two additional weak-medium bands at 807 and 697 cm^{-1} serves to distinguish *iso*violanthrene from violanthrene in this region. These two molecules have an identical CH substitution pattern (each has two rings with four adjacent CH groups, and four rings with two adjacent CH groups, and two rings with a lone CH group). It would appear that the strong 748–738 and 751–739 cm^{-1} doublets are associated with the four adjacent CH groups, the strong band at 787–791 cm^{-1} with two adjacent CH groups, and the band at 875–876 cm^{-1} possibly with a lone CH group. The CH out-of-plane bending vibrations of the polynuclear quinones thus absorb at a slightly higher frequency (*c.* 15 cm^{-1}) than in the parent hydrocarbon.

The remaining five quinones studied form an unrelated series and the application of this mode of analysis of the bands occurring in the CH out-of-plane bending vibration region has been less successful. The absorption spectrum of pyranthrone (V), an extended quinone with eight condensed rings, has strong bands at 905, 896, 804, 768, and 734 cm^{-1}. The 896 cm^{-1} vibration may be associated with the presence of two rings with lone CH groups, the 804 cm^{-1} band with the two rings each with an adjacent pair of CH groups, leaving the 734 and/or the 768 cm^{-1} vibration to be correlated with the two sets of four adjacent CH groups.

However, 4,10-dibromoanthanthrone (VII), which contains no *ortho*-substituted rings, has very strong bands at 772 and 757 cm^{-1} as well as less intense bands at 904 and 715 cm^{-1}. The former band may be associated with the presence of lone CH groups.

4,4′-Dibenzanthronyl (VIII) has a very intense doublet at 764–759 cm^{-1} which may be due to the combined absorption of the two sets of three adjacent and two sets of four adjacent CH groups that occur in this molecule. No unambiguous assignment can be made to the two lone CH groups that are also present.

Flavanthrone (VI) has two rings each with an adjacent pair of CH groups and two rings each with four adjacent CH groups. There is a medium-strong band at 855 cm^{-1} which falls within the range for an adjacent pair of CH groups. A strong band at 725 cm^{-1}, although it falls outside ranges listed in Table 3,

may be associated with the two sets of four adjacent CH groups in the flavanthrone molecule.

Apart from a very strong band at 713 cm^{-1}, 2,2′-dimethyl 1,1′-dianthraquinoyl (IX) has only several relatively weaker bands in the 900–650 cm^{-1} region and no convincing correlations can be suggested.

Hence, although the range of this class of compound studied here is very limited, there is good evidence to suggest that for the extended polynuclear quinones (and the parent hydrocarbons) containing eight or nine condensed rings the prominent bands between 900 and 650 cm^{-1} are associated with CH out-of-plane vibrations and that these bands may be analysed in terms of the number of adjacent CH groups on each ring: the correlated regions fall well within the ranges summarized in Table 3. However, such correlations become less certain for the smaller condensed molecules and non-extended quinones, particularly in the absence of a detailed study of a series of substituted derivatives for each molecular species.

Finally, it has been noted that all the quinones studied have a strong absorption band between 686 and 713 cm^{-1} which has not been correlated with the CH out-of-plane bending vibration. Since the hydrocarbons violanthrene and *iso*violanthrene show only relatively weak absorption in this region, it is possible that the strong absorption is associated with some skeletal ring vibration involving the rings containing the quinone carbonyl groups. This band occurs below 700 cm^{-1} for most of the extended quinones studied (exceptions being *iso*dibenzanthrone (II), 705 cm^{-1}, and 4,10-dibromoanthanthrone (VII), 715 cm^{-1}). The non-extended quinones containing anthraquinone groups absorb nearer 713 cm^{-1}, that is, 2,2′-dimethyl 1,1′-dianthraquinoyl (IX) 713 cm^{-1}, as well as indanthrone 713 cm^{-1}, and dianthrimide 707 cm^{-1} (Durie, Lack, and Shannon, unpublished data).

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SYNTHESIS OF SOME SUBSTANCES RELATED TO *p*–NITROPHENYL–β–GLUCOSIDE AND OF 4–*O*–METHYL GLUCOSE THROUGH CRYSTALLINE INTERMEDIATES

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Summary

The four monomethyl ethers of *p*-nitrophenyl-β-D-glucopyranoside have been synthesized, together with some other substances structurally related to the nitrophenyl glucoside. Their properties and those of the intermediates are reported. 4-*O*-Methyl glucose has been prepared by a method that uses only crystalline intermediates.

I. Introduction

To test a hypothesis of the author on the substrate specificity of the β-glucosidases of *Stachybotrys atra*, it was necessary to prepare a number of substances related to *p*-nitrophenyl-β-glucoside. The present paper reports the synthesis and properties of some of these compounds and of intermediates in their preparation.

No detailed discussion of the experimental procedures used will be given as they follow established practice and no question arises of any new principles in carbohydrate chemistry. The 3-*O*-methyl and 6-*O*-methyl derivatives were prepared by the Helferich reaction, using conditions found satisfactory for the synthesis of *p*-nitrophenyl-β-glucoside (Jermyn 1955). The reaction between *p*-nitrophenol and tetra-acetyl 6-methyl glucose gave yields of the same order as those reported by Jermyn (1955) for the reaction between *p*-nitrophenol and penta-acetyl-β-glucose. For the non-crystalline tetra-acetyl 3-methyl glucose, the yield from this reaction was very low, nor was it much improved by preparing the also non-crystallizable acetobromo-derivative as a further intermediate for reaction with sodium *p*-nitrophenate. Neither of these two syntheses of triacetyl 3-methyl *p*-nitrophenyl-β-glucoside is satisfactory for the production of more than the sample quantities needed for the purpose of this investigation, perhaps because steric factors oppose the formation of the desired anomers. Nevertheless, it is hard to devise a practicable synthesis starting from *p*-nitrophenyl-β-glucoside.

The synthesis of the 2-*O*-methyl derivative is remarkable only for the isolation of the intermediate 3,4,6-tri-*O*-acetyl 2-*O*-methyl-α-D-glucopyranosyl bromide as a crystalline hydrate. This compound (2-methyl acetobromoglucose) seems to be the first of its class to be isolated and the properties of 2-substituted glucoses are often widely different from those of their isomers. The fact that the monohydrate is a limiting composition remaining after the loss of a number of molecules

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of fairly tightly bound water, and is itself inherently unstable, suggests that it may be some kind of clathrate rather than a more highly organized type of molecular compound. The same opinion may well be hazarded for the group of three compounds found in series in the synthesis of the 4-*O*-methyl derivative. A great deal of difficulty was experienced in preparing analytically satisfactory samples with reproducible physical properties before it was realized that 4,6-benzylidene, 2,3-dibenzoyl-4,6-benzylidene, and 2,3-dibenzoyl *p*-nitrophenyl-β-glucosides all formed solvates with the recrystallization solvents with compositions varying according to the conditions of recrystallization. This was particularly the case for the dibenzoyl derivative where it proved impossible to prepare a solvate with a stoichiometric composition from any solvent. Since formation of the unsolvated compound involved melting the solvates and holding the melt at temperatures above 100 °C with consequent visible discoloration, it was finally analysed in the form of the solvate with the highest melting point and most reproducible properties, a non-stoichiometric complex with carbon tetrachloride.

Three compounds recorded here have structures that do not necessarily follow from synthetic procedures and structural proofs already reported in the literature. Of these the 6(?)-benzoyl and 6(?)-*p*-toluenesulphonyl derivatives of *p*-nitrophenyl-β-glucoside were obtained in such low yield from the reaction of the corresponding acid chlorides with *p*-nitrophenol in pyridine that the assumption of preferential substitution of the primary (6) hydroxyl group cannot be justified. Since they were too insoluble in water to be used as substrates for the β-glucosidase there did not seem to be any point in proving their structure as part of the present study, and the most probable structure is therefore no more than suggested here. Similarly, the by-product obtained in the synthesis of the 4-methyl derivative is merely recorded as the seemingly most probable structure, *p*-nitrophenyl 2,6(?)-dibenzoyl-β-glucoside, since its structure was irrelevant to the main purpose of the synthesis.

II. Experimental

All melting points are uncorrected. Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne.

(*a*) *2,3,4-Tri-O-acetyl 6-O-Methyl* p-*Nitrophenyl-β-*D*-glucopyranoside.*—6-*O*-Methyl glucose (10 g) was acetylated in the usual way with acetic anhydride and sodium acetate. To the crude, washed, air-dried product (8·3 g) was added an equal weight of *p*-nitrophenol and the mixture heated to 160 °C in a Woods metal bath. Powdered anhydrous $ZnCl_2$ (0·4 g) was now added, and heating at 160 °C under water-pump vacuum continued for 15 min. The hot reaction mixture was then dissolved in ethanol (65 ml). The crop of crystals formed on standing overnight was recrystallized from ethanol to give a yield of 1·69 g (17% on the acetyl compound). Further recrystallizations of a sample from ethanol gave white needles, m.p. 166–167 °C, $[\alpha]_D^{20}$ —25·8° (*c*, 1 in acetone) (Found: C, 51·5; H, 5·1; O, 39·1; N, 3·4; CH_3O, 7·2%. Calc. for $C_{19}H_{23}O_{11}N$: C, 51·7; H, 5·3; O, 39·9; N, 3·2; CH_3O, 7·0%).

(*b*) *6-O-Methyl* p-*Nitrophenyl-β-*D*-glucopyranoside Monohydrate.*—The above product (1·63 g) was dissolved in excess ethanol-benzene (2/1) and the bulk of the solvent distilled-off through a short column. A small piece of sodium was added to the anhydrous suspension, and the reaction mixture held 2 hr at room temperature after the last crystals had dissolved. A little acetic acid was now added and the solution evaporated to dryness. The residue was twice recrystallized from water to give 0·69 g (57%) of white needles, m.p. 103 °C, $[\alpha]_D^{20}$ —96·2° (*c*, 1 in ethanol-

water, 1/1) (Found: C, 47·2; H, 5·9; O, 42·6; N, 4·4; CH_3O, 9·3%. Calc. for $C_{13}H_{17}O_8N.H_2O$: C, 46·8; H, 5·7; O, 43·2; N, 4·2; CH_3O, 9·3%).

(c) *6-O-Methyl* p-*Nitrophenyl-α-D-glucopyranoside.*—The mother liquors from the preparation of the triacetyl β-anomer were diluted with benzene and then extracted successively with water and dilute NaOH solution, and the residue washed well with water. On taking this benzene solution to dryness under reduced pressure and dissolving in a little ethanol, further triacetyl β-anomer crystallized out (0·16 g). No other material could be induced to crystallize, and the solution was dehydrated and concentrated by adding benzene and ethanol and distilling off the solvent. Deacetylation as above for the β-anomer gave after a number of recrystallizations from water 0·40 g of white needles, m.p. 183 °C, $[\alpha]_D^{20}$ +214° (*c*, 1 in ethanol-water, 1/1) (Found: C, 49·4; H, 5·5; O, 41·1; N, 4·6; CH_3O, 9·8%. Calc. for $C_{13}H_{17}O_8N$: C, 49·5; H, 5·4; O, 40·6; N, 4·4; CH_3O, 9·8%).

(d) *6(?)-O-*p*-Toluenesulphonyl* p-*Nitrophenyl-β-D-glucopyranoside.*—*p*-Toluenesulphonyl chloride (7 g; slight excess) in chloroform (30 ml) was added slowly with stirring in the cold to *p*-nitrophenyl-β-glucoside (10 g) in anhydrous pyridine (100 ml). After standing 12 hr in the refrigerator, water (5 ml) was added, and after a further 1 hr the reaction mixture was poured into a mixture of chloroform and ice-water. The chloroform layer was washed with ice-cold dilute H_2SO_4, until the washings were acid to Congo red, and then with water. The solution was then dried with anhydrous $MgSO_4$ and the solvent removed by distillation under reduced pressure. The rubbery residue could not be purified by crystallization from organic solvents. After six recrystallizations from 1–2 l. of boiling water, with removal of most of the undissolved material in the first few recrystallizations, the yield was 0·7 g of long white needles, m.p. 156 °C (decomp.), $[\alpha]_D^{35}$ —33·5° (*c*, 1·6 in ethanol-water, 1/1) (Found: C, 50·5; H, 4·6; O, 35·3; N, 2·6; S, 7·3%. Calc. for $C_{19}H_{21}O_{10}NS$: C, 50·1; H, 4·7; O, 35·1; N, 3·1; S, 7·0%).

(e) *6(?)-O-Benzoyl* p-*Nitrophenyl-β-D-glucopyranoside Monohydrate.*—The above reaction was repeated except that the *p*-toluenesulphonyl chloride was replaced by 4·5 ml of benzoyl chloride. The semicrystalline product (2·0 g), after three recrystallizations from water, gave white needles, m.p. 177 °C, $[\alpha]_D^{20}$ —37° (*c*, 1 in ethanol-water, 1/1) (Found: C, 54·1; H, 4·8%. Calc. for $C_{19}H_{19}O_9N.H_2O$: C, 53·9; H, 5·0%).

(f) *4,6-O-Benzylidene* p-*Nitrophenyl-β-D-glucopyranoside.*—*p*-Nitrophenyl-β-glucoside (60·2 g; 0·2 mole), anhydrous powdered $ZnCl_2$ (56 g), and benzaldehyde (200 ml) were shaken together for 3 hr at room temperature and then poured into a mixture of ice-water (1 l.) and light petroleum (b.p. 40–60 °C; 500 ml). The product solidified immediately and was filtered-off and washed exhaustively with ice-water and light petroleum. It was recrystallized from ethanol (3 l.) as yellowish needles (62·3 g, 80%). Multiple recrystallizations from ethanol gave white needles, m.p. 184–185 °C, $[\alpha]_D^{20}$ —44·9° (*c*, 2 in acetone) (Found (product equilibrated with ethanol in a desiccator): C, 57·6; H, 5·8; O, 33·0; N, 3·6%. Calc. for $C_{19}H_{19}O_8N.C_2H_5OH$: C, 57·9; H, 5·8; O, 33·1; N, 3·2%).

Drying this compound *in vacuo* or at oven temperatures below 100 °C gave products with analyses intermediate between that given above and that expected for the unsolvated compound, although the apparent m.p. was constant at 184–185 °C, which appears to be that of the unsolvated compound.

(g) *2,3-Di-O-benzoyl 4,6-O-Benzylidene* p-*Nitrophenyl-β-D-glucopyranoside.*—The oven-dried, partially solvated product above (58·8 g) was dissolved in anhydrous pyridine (440 ml) and benzoyl chloride (50 ml; 3 molar proportions) was added. The mixture was kept at 37 °C for 6 days. Water (10 ml) was added, and after 1 hr further, the mixture was poured into a large excess of water. The crystalline product was filtered off, washed exhaustively with water, and recrystallized from acetone (2 l.) to give 66·7 g of white needles. Cautious addition of water to the filtrate gave a further 20·4 g. Total yield, 87·1 g (96% apparent).

Recrystallized from acetone, the compound had m.p. 192 °C, resolidifying to melt at 217 °C. Intensively oven-dried at 100 °C, it had m.p. 217 °C directly, $[\alpha]_D^{20}$ +80·2° (*c*, 0·4 in acetone) Found: C, 66·2; H, 4·7; O, 26·7; N, 2·5%. Calc. for $C_{33}H_{27}O_{10}N$: C, 66·3; H, 4·6; O, 26·8; N, 2·3%).

Recrystallized from ethanol, the compound had m.p. 232 °C, falling after 1 month's storage to 205–222 °C. On an open bar melting-point apparatus, the m.p. was erratic, but appeared to be 217 °C if the sample had been heated sufficiently just below 200 °C (Found: C, 64·9; H, 4·7; O, 27·4; N, 2·6%. Calc. for $C_{33}H_{27}O_{10}N.C_2H_5OH$: C, 65·3; H, 5·1; O, 27·3; N, 2·2%). It appears that the unsolvated compound melts at 217 °C, and the acetone and ethanol solvates at 192 and 232 °C respectively.

(*h*) *2,3-Di-*O*-benzoyl* p-*Nitrophenyl-β-*D*-glucopyranoside*.—The acetone-solvated product (86·7 g) was dissolved in boiling acetone (900 ml), N HCl (100 ml) added, and boiling continued 4 hr. The precipitate had all redissolved after 0·5 hr. The solution was then cooled and poured into excess of water. The sticky semicrystalline precipitate was triturated with benzene and the solid product filtered and washed well with benzene and water in turn. Recrystallization from ethyl acetate-benzene gave 73·2 g of white needles, m.p. 70–80 °C, resolidifying to melt at 155–160 °C.

This compound gave solvates with every recrystallization solvent tried, some with very low m.p., but agreeing in giving a second m.p. at 159–160 °C, which is apparently that of the unsolvated compound. The analytical sample was of the carbon tetrachloride complex, which had perfectly reproducible properties and was quite stable to vacuum drying over P_2O_5 and paraffin wax, but was nevertheless apparently not a stoichiometric compound. It had m.p. 95–96 °C, resolidifying to melt at 159–160 °C, $[\alpha]_D^{23}$ +79·1° (*c*, 2·8 in acetone) (Found: C, 46·4; H, 3·4; O, 22·3; Cl, 25·7; volatile at 100 °C, 27·1%. Calc. for $C_{26}H_{23}O_{20}N$, 1·28 CCl_4: C, 46·4; H, 3·3; O, 22·6; Cl, 25·7; CCl_4, 27·8%).

(*i*) *2,3,6-Tri-*O*-benzoyl* p-*Nitrophenyl-β-*D*-glucopyranoside*.—The crude benzene-solvated product above (66·3 g) was dissolved in anhydrous pyridine (700 ml) and benzoyl chloride (22 ml; 1·4 molar proportions) in chloroform (120 ml) was added with stirring over 25 min, the mixture being held at room temperature by water cooling. After 4 hr at room temperature, water (25 ml) was added and then after 1 hr further, chloroform (500 ml) and a large excess of ice-water. The chloroform layer was washed with ice-water and then with a large volume of ice-cold dilute H_2SO_4. As soon as the pyridine had been removed, the chloroform layer deposited solid. The crystalline material was filtered off and washed with ice-water and chloroform. Concentration of the washed, dried chloroform layer from the filtrate, and recrystallization of the residue from a little cold chloroform gave further product, yield 41·5+10·7 g (52·2 g, 65%) of essentially pure product. Recrystallization from aqueous acetone gave white needles, m.p. 204–205 °C, $[\alpha]_D^{25}$ +57·9° (*c*, 2·4 in acetone) (Found: C, 64·8; H, 4·7; O, 28·5; N, 2·3%. Calc. for $C_{33}H_{27}O_{11}N$: C, 64·6; H, 4·4; O, 28·7; N, 2·3%).

(*j*) *2,6(?)-Di-*O*-benzoyl* p-*Nitrophenyl-β-*D*-glucopyranoside*.—An attempt to methylate the above product with methyl iodide and moist silver oxide according to directions of Hodge and Rist (1952*b*) gave unchanged starting material. When a further attempt was made to force the reaction by heating a mixture of the tribenzoyl compound (9·0 g), methyl iodide (40 ml), and silver oxide (16 g) at the b.p. of methyl iodide for 2 hr, a residue (2·9 g) was left after the reaction mixture had been extracted successively with boiling chloroform and aqueous KCN solution. Unchanged starting material (3·6 g) was recovered from the chloroform extract.

Recrystallization of the residual material from acetone gave white needles of a methoxyl-free compound analysing for a dibenzoyl nitrophenyl glucose, m.p. 244 °C, $[\alpha]_D^{22}$ —1·9° (*c*, 2 in acetone) (Found: C, 61·3; H, 4·7; O, 30·9; N, 2·8%. Calc. for $C_{26}H_{23}O_{10}N$: C, 61·3; H, 4·6; O, 31·4; N, 2·8%). This compound is tentatively identified as the 2,6-dibenzoyl compound since it is different from the 2,3-compound, and the 3-benzoyl group next to the unsubstituted 4-hydroxyl group would be expected to be the one removed in any anomalous displacement reaction.

(*k*) *2,3,6-Tri-*O*-benzoyl 4-*O*-Methyl* p-*Nitrophenyl-β-*D*-glucopyranoside*.—Since the above result was believed to be partially due to the insolubility of the tribenzoyl nitrophenyl glucoside in methyl iodide, a search was made for a solvent in which the compound was freely soluble but that would not be affected by the methylation procedure. Dioxan fulfilled these requirements, but the reaction products were the above dibenzoyl compound, an ethanol-soluble syrup, and a small

amount of crystalline material more soluble in ethanol than the dibenzoyl compound, but with a methoxyl content too low (2·3%) to be the required fully-methylated product.

Methylation in dimethylformamide according to Kühn, Trischmann, and Löw (1955) was next tried and gave a rather low yield of the desired product. Tribenzoyl nitrophenyl glucoside (6·1 g) was dissolved in dimethylformamide (25 ml) and methyl iodide (5 ml). Silver oxide (5 g) was added in portions over 15 min with rapid stirring. The temperature of the reaction mixture only rose a degree or two above room temperature (25 °C). After 20 min further stirring, the reaction flask was shaken mechanically for 40 hr. The silver salts were filtered off and washed with dimethylformamide and chloroform. The combined filtrate and washings were evaporated to dryness under reduced pressure and the product extracted with hot chloroform. An insoluble silver-containing residue was left. The chloroform solution was evaporated under reduced pressure and the product dissolved in hot ethanol (50 ml). There was immediate deposition of white needles (2·1 g, 33% yield). Further recrystallization from aqueous acetone gave white needles, m.p. 197 °C, $[\alpha]_D^{20}$ +55·8° (*c*, 2 in acetone) (Found : C, 64·8 ; H, 4·7 ; O, 28·2 ; N, 2·4 ; CH_3O, 5·0%. Calc. for $C_{34}H_{29}O_{11}N$: C, 65·1 ; H, 4·7 ; O, 28·0 ; N, 2·2 ; CH_3O, 4·9%). Although very similar to the starting material in physical properties, it gave large depressions of the m.p. in admixture with it.

Fractionation of the ethanol-soluble material gave considerable amounts of the low-methoxyl substance mentioned above, m.p. 172 °C, which is apparently some kind of molecular compound, together with a syrup that could not be induced to crystallize.

(*l*) *4-*O*-Methyl* p-*Nitrophenyl-β-*D*-glucopyranoside*.—The methylated tribenzoyl glucoside (1·5 g) was catalytically debenzoylated by sodium in ethanol and the product recrystallized from water to give 0·61 g (80%) of white needles. Further recrystallizations from water gave a product, m.p. 189 °C, $[\alpha]_D^{20}$ —93·5° (*c*, 1 in ethanol-water, 1/1) (Found : C, 49·6 ; H, 5·4 ; O, 40·8 ; N, 4·2 ; CH_3O, 9·4%. Calc. for $C_{13}H_{17}O_8N$: C, 49·5 ; H, 5·4 ; O, 40·6 ; N, 4·4 ; CH_3O, 9·8%).

It would be unwise to assume the orientation of either of the preceding compounds on the basis of earlier work (Levene and Raymond 1932) since the conditions that were used in the methylation might perhaps lead to migration of the benzoyl groups. A sample of the supposed 4-methyl nitrophenyl glucoside (0·2 g) was therefore hydrolysed with 0·5N HCl (5 ml ; 2 hr under reflux) and the resulting solution passed down a column of " Bio-Deminrolit ". The combined effluent and washings when analysed for reducing sugar showed an almost 100% recovery of methyl glucose. The solution of methyl glucose was reduced to small volume and heated in a water-bath after the addition of phenylhydrazine hydrochloride and sodium acetate. The resulting yellow precipitate after several recrystallizations from aqueous ethanol had physical constants, m.p. 158 °C, $[\alpha]_D^{20}$ (equil.) —13° (*c*, 1 in ethanol), nearly agreeing with those reported in the literature (Bourne and Peat 1950) for 4-*O*-methyl glucosazone. The expected orientation is thus confirmed.

The methylation procedure was used to prepare further amounts of 4-*O*-methyl glucose which was handled in solution since, in agreement with all previous work on this substance it could not be induced to crystallize. It is noteworthy that this appears to be the first synthesis of 4-*O*-methyl glucose from glucose proceeding entirely through crystalline intermediates.

(*m*) *2,3,4,6-Tetra-*O*-acetyl* p-*Nitrophenyl-β-*D*-thioglucopyranoside*.—To a freshly prepared solution of *p*-nitrothiophenol (35 g) in acetone (400 ml) and water (200 ml) containing 1 equiv of NaOH was added in a rapid stream with stirring a solution of acetobromoglucose in chloroform (200 ml), prepared from glucose (50 g) according to the directions of Barczai-Martos and Korosy (1950). No attempt was made to keep the reaction mixture cool and stirring was continued 0·5 hr after the addition was complete. The crystalline product was filtered off, the filtrate diluted with water, and the washed and dried chloroform layer concentrated *in vacuo*. The residue was crystallized from a little aqueous acetone. Recrystallization of the bulked products gave 25 g (18% yield on glucose) of yellowish needles. Several recrystallizations from aqueous acetone gave white needles, m.p. 180–181 °C, $[\alpha]_D^{20}$ +23·0° (*c*, 5 in chloroform) (Found : C, 49·6 ; H, 4·8 ; S, 6·5%. Calc. for $C_{20}H_{23}O_{11}NS$: C, 49·5 ; H, 4·8 ; S, 6·6%).

(*n*) p-*Nitrophenyl*-β-D-*thioglucopyranoside Monohydrate*.—Catalytic deacetylation of the above product with sodium in anhydrous ethanol gave nearly quantitative yields of the thioglycoside. Recrystallization from water gave white needles, rapidly yellowing on storage, m.p. 160 °C, $[\alpha]_D^{20}$ —106·5° (*c*, anhydrous compound, 5 in ethanol-water, 1/1) (Found: C, 42·8; H, 5·2; O, 38·0; N, 4·0; S, 9·8; volatile *in vacuo* at 80 °C, 4·7%. Calc. for $C_{12}H_{15}O_7NS.H_2O$: C, 43·0; H, 5·1; O, 38·2; N, 4·2; S, 9·6; H_2O, 5·3%).

(*o*) *2,4,6-Tri*-O-*acetyl 3*-O-*Methyl* p-*Nitrophenyl*-β-D-*glucopyranoside*.—(i) *Via the Helferich Reaction*. When 3-*O*-methyl glucose (3 g) was acetylated with sodium acetate and acetic anhydride, no crystalline product was obtained on pouring the reaction mixture into excess water. The suspension of syrup was extracted with chloroform and the chloroform extract washed successively with cold KOH solution and water and dried. Evaporation under reduced pressure gave 3 g of syrup. This was mixed with *p*-nitrophenol (3 g), and heated for 15 min at 160 °C under reduced pressure in the presence of powdered anhydrous $ZnCl_2$ (0·3 g). A solution of the reaction mixture in ethanol deposited no crystals on standing; therefore, it was diluted with benzene and extracted successively with water and excess dilute NaOH solution. Excess ethanol was then added and the whole solution evaporated to dryness under reduced pressure. A solution of the resulting syrup in a little ethanol gave a crystalline deposit on standing. Two recrystallizations of this material from ethanol gave 50 mg of white needles, m.p. 137 °C, $[\alpha]_D^{25}$ —20° (*c*, 1 in chloroform) (Found: C, 52·0; H, 5·2%. Calc. for $C_{19}H_{23}O_{11}N$: C, 51·7; H, 5·2%).

An attempt to carry out a similar synthesis with 2-*O*-methyl glucose gave no crystalline product.

(ii) *Via the Acetobromo-Derivative of 3*-O-*Methyl Glucose*. To 3-*O*-methyl glucose (0·5 g) suspended in acetic anhydride (3 ml) was added a micro-drop of perchloric acid. When the heat of the reaction had subsided, the solution was allowed to stand 30 min and a 25% (w/v) solution of HBr in glacial acetic acid (10 ml) then added. After 1 hr further the solution was poured into ice-water-chloroform and worked up in the usual way. The final syrup was dissolved in acetone (5 ml) and a solution of 0·36 g of *p*-nitrophenol in acetone (2·5 ml) and N KOH (2·5 ml) added. After standing 12 hr, the acetone was removed under reduced pressure and the residue cooled and washed with ice-water. Recrystallization from a little methanol gave 48 mg (6%) of white needles identical in physical properties with those obtained by method (i) above.

(*p*) *3*-O-*Methyl* p-*Nitrophenyl*-β-D-*glucopyranoside*.—Catalytic deacetylation of the above compound by sodium in ethanol, and recrystallization from water gave white needles, m.p. 137 °C, $[\alpha]_D^{25}$ —70° (*c*, 0·6 in ethanol-water, 1/1) (Found: C, 49·2; H, 5·3%. Calc. for $C_{13}H_{17}O_8N$: C, 49·5; H, 5·4%).

(*q*) *4,6*-O-*Ethylidene 2,3*-O-*Oxydiethylidene* p-*Nitrophenyl*-β-D-*glucopyranoside*.—Since it seemed probable that 4,6-ethylidene *p*-nitrophenyl-β-glucoside would be useful (by way of its 2,3-dinitrate) as an intermediate in the synthesis of 2-*O*-methyl *p*-nitrophenyl-β-glucoside, an attempt was made to synthesize this compound directly. *p*-Nitrophenyl-β-glucoside (8 g), paraldehyde (20 ml), and concentrated HCl (1·5 ml) were shaken 3 hr at room temperature. During this period the mixture liquefied with solution of the glucoside and then set solid. The product was triturated with water, filtered, and washed with water until the washings were neutral. It was then recrystallized from ethanol to give white needles (6 g), which analysis of a sample repeatedly recrystallized from ethanol showed to be the 2,3-oxydiethylidene compound, m.p. 234 °C, $[\alpha]_D^{35}$ —69·5 (*c*, 1·3 in acetone) (Found: C, 54·3; H, 5·8; O, 36·0; N, 3·6%. Calc. for $C_{18}H_{23}O_9N$: C, 54·4; H, 5·8; O, 36·2; N, 3·5%). Neither the mother liquors from the recrystallization nor a chloroform extract of the water washings could be made to yield a second crystalline compound corresponding to the expected simple 4,6-ethylidene derivative.

(*r*) *3,4,6-Tri*-O-*acetyl 2*-O-*Methyl*-α-D-*glucopyranosyl Bromide*.—The compound *N*-(3,4,6-tri-*O*-acetyl 2-*O*-methyl-D-glucopyranosyl) piperidine, an intermediate in the most practical synthesis of 2-*O*-methyl glucose (Hodge and Rist 1952*b*), appeared to be a suitable starting material for the preparation of 2-*O*-methylglucosides. Attempts to replace the piperidyl group by a bromo-group through the direct action of HBr in glacial acetic acid gave syrupy products that could neither be induced to crystallize nor to give crystalline reaction products with *p*-nitrophenol.

However, the bromo-derivative could be prepared via the non-crystalline 1-hydroxyl compound as follows.

The piperidine compound (28 g) was shaken 3 hr at room temperature with 0·5N HCl (140 ml; slightly less than an equimolar proportion) and the solution then heated 1 hr at 80 °C. After cooling and filtering off a little unreacted material, the product was evaporated under reduced pressure and acetone and then ether distilled from it a number of times to dehydrate it. Piperidine hydrochloride was removed from the final ethereal suspension by filtration, but no crystalline product could be recovered from the filtrate either by the method described by Hodge and Rist (1952*a*) for the preparation of tetra-acetyl glucose or otherwise.

The ethereal solution was taken to dryness under reduced pressure and of a solution of HBr in glacial acetic acid (25% w/v; 200 ml) added to the residue. After 1 hr, the solution was poured into ice-water-chloroform and worked up in the usual way. The final syrup was dissolved in an equal volume of ether and induced to crystallize by seeding with dry ice and scratching. The resulting solid product was washed with a little cold ether and recrystallized from ether. Yield of brownish needles, 10·2 g. A further 5·0 g could be recovered in a number of successive crops by working up the mother liquors. Total yield, 15·2 g (55%). Further recrystallizations from ether gave white needles, m.p. 86 °C, softening over a range of 15–20 °C below this temperature, $[\alpha]_D^{27}$ +232° (*c*, 5 in chloroform) (Found: C, 38·6; H, 5·4; O, 35·9; Br, 19·6%. Calc. for $C_{13}H_{19}O_8Br.H_2O$: C, 38·9; H, 5·3; O, 35·9; Br, 19·9%). The method of preparation of the analytical sample (recrystallization from undried ether and drying *in vacuo* over KOH) has thus left the compound as a hydrate since the analytical values vary in the opposite direction from those expected for partial hydrolysis, and the compound reacted normally.

As first prepared, the compound contained approximately 5 mol of water for every mol of the bromide, and the water content fell slowly until the monohydrate ratio was reached. The monohydrate was not stable indefinitely to storage *in vacuo* and after a few days was observed first to give low figures for bromine on analysis and then to break down to a tarry liquid.

The configuration of this compound is deduced from its optical rotation and the known relative stabilities of the acetobromoglycoses.

(*s*) *3,4,6-Tri-O-acetyl 2-O-Methyl* p-*Nitrophenyl-β-D-glucopyranoside.*—To 2-methylacetobromoglucose (11·5 g) dissolved in acetone (50 ml) was added a mixture of *p*-nitrophenol (4·2 g) dissolved in acetone (35 ml) and 2N KOH (15 ml). The combined solutions were allowed to stand at room temperature (5 hr) and the acetone then removed by distillation under reduced pressure. The residue became semicrystalline after washing with several changes of ice-water and a crystalline product was obtained by dissolving it in methanol (50 g), allowing the solution to cool, and washing the product with cold methanol-water (3/1); yield, 5·6 g (42%). Two recrystallizations from ethanol gave white needles, m.p. 131 °C, $[\alpha]_D^{25}$ —34·2° (*c*, 3·5 in acetone) (Found: C, 51·7; H, 5·1; O, 39·5; N, 3·7; CH_3O, 7·1%. Calc. for $C_{19}H_{23}NO_{11}$: C, 51·7; H, 5·2; O, 39·9; N, 3·2; CH_3O, 7·0%). The configuration is deduced from the optical rotation and the known stereochemistry of the replacement reaction.

(*t*) *2-O-Methyl* p-*Nitrophenyl-β-D-glucopyranoside.*—Triacetyl 2-methyl *p*-nitrophenyl-β-glucoside (4·4 g) was catalytically deacetylated by sodium in ethanol and the product recrystallized from water; yielding yellowish needles 2·2 g (70%). Further recrystallizations from water gave white needles, m.p. 178–179 °C, $[\alpha]_D^{23}$ —90·2° (*c*, 4 in ethanol-water, 1/1) (Found: C, 49·8; H, 5·6; O, 40·2; N, 4·6; OCH_3, 9·8%. Calc. for $C_{13}H_{17}O_8N$: C, 49·5; H, 5·4; O, 40·6; N, 4·4; CH_3O, 9·8%).

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SEPARATION OF MONOMETHYLATED *p*-NITROPHENYL-β-GLUCOSIDES ON A CARBON COLUMN

By M. A. Jermyn*

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Summary

The gradient elution of *p*-nitrophenyl-β-D-glucopyranoside and its four monomethyl ethers from a carbon column has been investigated. It does not appear possible to separate the monomethyl ethers from each other by this method.

I. Introduction

In two previous papers the author has discussed the separation of glucosides by gradient elution from a carbon column (Jermyn 1957*a*) and the synthesis of the monomethyl ethers of *p*-nitrophenyl-β-D-glucopyranoside (Jermyn 1957***b***). Since the synthesis of these latter was tedious but had rendered them available as marker compounds, it seemed profitable to investigate whether the reaction mixture from the monomethylation of *p*-nitrophenyl-β-glucoside could be fractionated to give the individual components in a single step. Since the relative reactivity of the various positions around the glucopyranose ring during such substitution reactions has been little investigated, such a study should also give valuable information about chemical mechanisms.

II. Experimental

(*a*) *Methylation*

The methylation procedure (methyl iodide and silver oxide in dimethyl formamide) was essentially that of Kühn, Trischmann and Löw (1955). When excess methyl iodide was used this method gave almost quantitative yields of 2,3,4,6-tetra-*O*-methyl *p*-nitrophenyl-β-D-glucopyranoside.

*2,3,4,6-Tetra-*O*-methyl* p-*Nitrophenyl-β-D-glucopyranoside.*—*p*-Nitrophenyl-β-glucoside (3·0 g; 0·01 mol) was dissolved in dimethylformamide (20 ml). Methyl iodide (5 ml; 0·08 mol) was added and then silver oxide (10 g) in one portion. The reaction mixture was shaken overnight and no attempt was made to moderate the exothermic reaction that set in after 20 min. It was then filtered and the residue washed successively with dimethylformamide and chloroform. The combined filtrate and washings were evaporated to dryness under reduced pressure. The residue was dissolved in hot chloroform and the solution, after filtering off some insoluble silver compounds, evaporated to dryness. Yield of yellow solid, 3·5 g (98% of the crude tetramethyl ether). Recrystallization from ethanol-water (2/1) gave 3·15 g of white needles plus 0·25 g further of less pure material from the mother liquors. Further recrystallization from methanol gave long white needles, m.p. 110 °C, $[\alpha]_D^{23}$ —124·3° (*c*, 3·3 in chloroform) (Found: C, 54·2; H, 6·5; O, 35·2; N, 4·2; CH_3O, 34·3%. Calc. for $C_{12}O_{11}O_4N(OCH_3)_4$: C, 53·8; H, 6·5; O, 35·8; N, 3·9; CH_3O, 34·8%).

In a typical monomethylation experiment, *p*-nitrophenyl-β-glucoside (1·5 g; 0·005 mol) was dissolved in freshly-distilled dimethylformamide (10 ml) and methyl iodide (0·31 ml; 0·005 mol) and silver oxide (3·5 g; 0·015 mol) added. The stoppered flask was shaken for

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3 days at room temperature and the contents then worked up as described above. The non-crystalline residue was dissolved in 25 ml of hot water to which a drop of acetic acid had been added. A small amount of tarry material remained undissolved.

(b) Column Operation

The operation of the " small column " has been described previously (Jermyn 1957*a*). Throughout these experiments the column temperature was maintained at 28 °C, and the column charge at 15 g. The solubility of air in the *n*-butanol–acetone mixture supplied to the mixing chamber was so much higher than its solubility in water that major difficulties arose through gas evolution in the chamber and column, even when the acetone and butanol had been separately boiled to rid them of air. The apparatus was therefore modified by fitting to the mixing chamber a vent tube rising above the level of the supply vessel. The chamber was enclosed in a heating jacket to keep its temperature (35–40 °C) somewhat above that of the column.

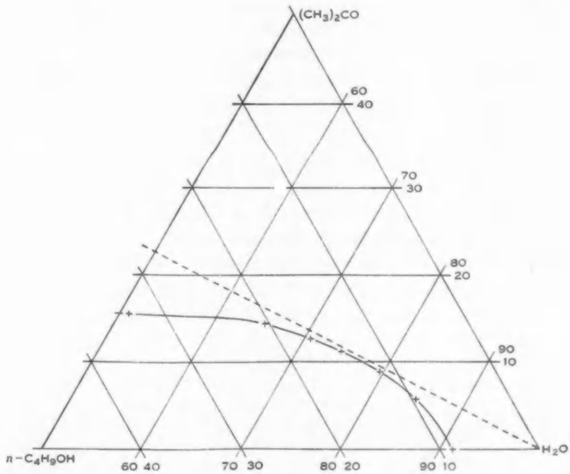

Fig. 1.—Portion of the phase diagram for the system *n*-butanol–acetone–water at 28 °C. Determined with laboratory reagent grade solvents by adding varying amounts of water to an acetone–butanol (40 : 60) mixture and titrating the two phases to miscibility with acetone–water (30/70). All results expressed in volume per cent. — — represents the path of composition change as acetone–butanol (45/55) is added to water.

The earlier work had shown that *p*-nitrophenyl-β-glucoside was only slowly eluted from " Darco G-60 " charcoal by an ethanol gradient (Jermyn 1957*a*). Since *n*-butanol and the higher normal aliphatic alcohols are not sufficiently soluble in water to give a suitably steep concentration gradient, it was necessary to use a " carrier " to promote miscibility. Of the three most attractive possibilities, namely, methanol, ethanol, and acetone, it was found that acetone was effective in each case at the lowest concentration as a carrier for *n*-butanol, *n*-pentanol, and *n*-hexanol. Since the mixtures capable of infinite dilution with water without phase separation contained over 80 per cent. and over 90 per cent. of acetone respectively for *n*-pentanol and *n*-hexanol, *n*-butanol–acetone mixture was used in this work. Examination of Figure 1 shows that a mixture of acetone–butanol (45/55) can be added indefinitely to water without phase separation. This mixture was therefore used throughout this investigation.

(c) *Analysis of Fractions*

p-Nitrophenyl-β-glucoside and its derivatives could be determined at very great dilutions by taking advantage of their ready alkaline hydrolysis. The sample to be tested (1 ml) and N NaOH (2 ml) were mixed in a test tube and heated in a boiling water-bath (10 min); experiment showed that this time was ample for the complete hydrolysis of the few mg quantities involved. The cooled hydrolysate was diluted to 10 ml and the optical density at 4000 Å determined. Concentrations of 10^{-6}M (0·3 μg/ml) are readily measured by this technique.

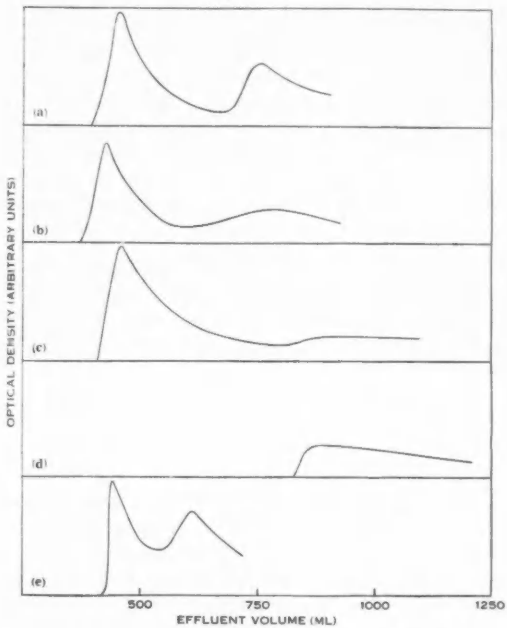

Fig. 2.—Separation by gradient elution of *p*-nitrophenyl-β-glucoside and mono-*O*-methyl *p*-nitrophenyl-β-glucosides from "Darco G-60" carbon-cellulose (15 g of 1/1) at 28 °C in the "small column". Feed to mixing chamber, acetone–*n*-butanol (45/55). (*a*) 4-methyl (6+6 mg); (*b*) 6-methyl (3+3 mg); (*c*) 2-methyl (3+3 mg); (*d*) 2-methyl alone (3 mg); (*e*) 3-methyl (3+3 mg).

This procedure failed completely for the 2-methyl ether, and the resistance of this compound to alkaline hydrolysis has certain important theoretical consequences that will be dealt with elsewhere. Since the use of acid hydrolysis, especially for highly butanolic fractions, introduced a number of complications, a form of drastic alkaline hydrolysis was used instead. To the fraction (2 ml) was added 50% NaOH solution (2 ml) and the whole evaporated in an oven at 100 °C for 6 hr. After dilution of the residue to 10 ml, the colour was red as before. This method is tedious but sodium *p*-nitrophenate is apparently resistant to such concentrated alkali indefinitely, and *p*-nitrophenyl-β-glucoside and all its monomethyl ethers can thus be determined under identical conditions.

III. Results

Once the elution volume for the *p*-nitrophenyl-β-glucoside peak had been determined, it was then possible to determine the position of the peaks for the separate monomethyl *p*-nitrophenyl-β-glucosides and to assess the ease of

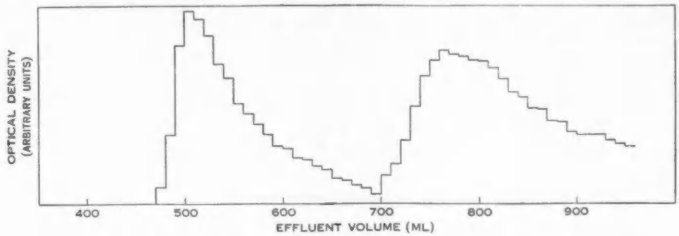

Fig. 3.—Separation by gradient elution of *p*-nitrophenyl-β-glucoside (3 mg) and 2-*O*-methyl, 4-*O*-methyl, and 6-*O*-methyl *p*-nitrophenyl-β-glucosides (3 mg of each). Same conditions as in Figure 2.

separation from the parent compound. Figure 2 shows the separation of *p*-nitrophenyl-β-glucoside from single monomethyl derivatives ; Figure 3, its separation from a mixture of three monomethyl derivatives ; and Figure 4, the fractionation of a "monomethylation" product prepared under the conditions described above.

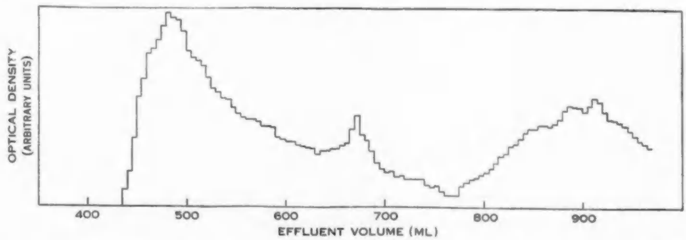

Fig. 4.—Fractionation of volume of "monomethylation" product solution equivalent to 12 mg of original *p*-nitrophenyl-β-glucoside. Same conditions as in Figure 2. Comparison of the totalled optical densities of the fractions with that of a suitable dilution of the starting material showed that at least 90 per cent. of the original *p*-nitrophenyl content had been eluted when the experiment was terminated.

IV. Discussion

The result shown in Figure 4 (3-day reaction time) was not much altered by using shorter (30-hr) or longer (10-day) reaction times. From this observation and the considerable heat evolution in permethylation experiments both as reported here and by Kühn, Trischmann and Löw (1956) it may be deduced that the methylation reaction in fact takes place quite rapidly and that the "unreacted" methyl iodide that must be postulated to account for the methylation of not more than about half of the glucoside is in fact rapidly destroyed by acceleration in the presence of silver oxide of the normally slow decomposition

of methyl iodide dissolved in dimethyl formamide (Kornblum and Blackwood 1956).

It is apparent from the form of Figure 4 that every position around the glucopyranose ring has been methylated to some degree under the conditions used. The poor separation of the reaction products does not allow more than this qualitative statement to be made.

Viewed purely as an attempt to separate the methylated *p*-nitrophenyl-β-glucosides, the experiments set out here would be scarcely worth recording except as an incidental failure. However, they do illuminate certain further limitations to the gradient elution technique that were not readily apparent in experiments using the weakly adsorbed sugars and less potent eluants than butanol. The points enumerated below are apparent when studying Figures 2–4, and (ii) may be readily deduced from the principles governing gradient elution set out in an earlier paper (Jermyn 1957*a*).

(i) As the adsorbands become more strongly held and the eluants needed to remove them correspondingly more potent, it becomes harder to get consistent performance of the column from experiment to experiment. Compare the erratic position of the *p*-nitrophenyl-β-glucoside peak eluted by *n*-butanol with the constant position of disaccharide peaks eluted by ethanol.

(ii) As the affinity of the column material for the adsorband increases, the bandwidth for a given amount of material also increases. Thus the bandwidth for 25 mg of *p*-nitrophenyl-β-glucose is 240 ml ; for 3 mg, 100 ml. For comparison, the bandwidth for 25 mg of lactose in the present system is about 5 ml. Hence, the amount of material that can be put on the column to take advantage of the available separation between peaks is severely limited. The amount used for the present glucosides (3 mg per component) is obviously well above the optimum. We may generalize these observations by remarking that as the affinity of the column material for a pair of adsorbands increases, so must the difference in adsorption properties between them if they are to be satisfactorily separated by gradient elution. It does not appear that use of different eluting agents or gradients would much improve the appearance of Figure 3.

(iii) The earlier experiments (Jermyn 1957*a*) showed that as elution conditions are varied so that the peak for a given amount of a certain adsorband appears at progressively greater effluent volumes, the peak flattens and the bandwidth increases. The present work shows that this cannot be generalized for a series of absorbands. The sharpness of the peaks for the monomethyl compounds ($3,4 > 6 > 2$) bears no obvious relation to their elution volume. The general rules for the shape of adsorband peaks on a gradient elution column apparently merely modify a characteristic behaviour for a given adsorband. Indeed the bandwidth for identical amounts with identical peak position could only be expected to be also identical if the slopes of the adsorption isotherms for the different adsorbands were identical which is not in fact the case.

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OXIDATIONS WITH IODOSOBENZENE DIACETATE[*]

VII. THE OXIDATION OF *p*-NITRO-*N*-METHYLANILINE

By JOAN MITCHELL[†] and K. H. PAUSACKER[†]

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Summary

The reaction of *p*-nitro-*N*-methylaniline with iodosobenzene diacetate has been investigated in both benzene and acetic acid solution. The relative amount of the oxidant has been varied. The nature of the products indicates that extensive demethylation occurs.

Tetramethylbenzidine is formed when dimethylaniline is oxidized in benzene. The mechanisms of these reactions are discussed.

I. INTRODUCTION

Iodosobenzene diacetate has been used to oxidize a number of primary aromatic amines in both benzene and acetic acid solution. It has been found that azo-compounds are generally formed (Pausacker 1953; Barlin, Pausacker, and Riggs 1954). However, the oxidation of *o*-nitroanilines, in benzene solution, yields benzofurazan oxides (Pausacker 1953; Pausacker and Scroggie 1954) and the oxidation of β-naphthylamine (Barlin, Pausacker, and Riggs 1954), *p*-anisidine, and *p*-phenetidine (Mitchell and Pausacker 1954) yields, *inter alia*, quinonoid products.

The oxidation of *p*-nitro-*N*-methylaniline and *NN*-dimethylaniline with iodosobenzene diacetate is discussed in the present paper.

II. EXPERIMENTAL

(*a*) *Oxidation of* p-*Nitro*-N-*methylaniline*

(i) *Oxidation in Benzene Solution.*—*p*-Nitro-*N*-methylaniline (3·6 g), dissolved in benzene (300 ml), was added to a solution of iodosobenzene diacetate (7·7 g; 1 mole) in benzene (240 ml). After standing for 24 hr, the orange-red solution was filtered (insoluble material, 0·3 g), and the filtrate was concentrated to *c.* 100 ml by distillation under reduced pressure (20 mm). The resultant solution was chromatographed on alumina, and the following bands were eluted with benzene: (1) pale red; (2) deep orange; (3) orange. All three bands yielded some 4,4′-dinitroazobenzene (m.p. and mixed m.p. 221 °C) which was separated from the other components by means of fractional crystallization from ethanol. The total yield was 0·33 g (10 per cent.). After removing 4,4′-dinitroazobenzene, *N*-nitroso-*N*-methyl-4-nitroaniline was also obtained from band (1). It crystallized from *cyclo*hexane as cream needles (m.p. and mixed m.p. with an authentic specimen, 95 °C) (Found: C, 46·65; H, 3·7; N, 22·8; O, 25·7%; mol. wt., 187. Calc. for $C_7H_7N_3O_3$: C, 46·4; H, 3·9; N, 23·2; O, 26·5%; mol. wt., 181). The yield was 0·1 g (3%).

[*] For Part VI of this series see *J. Chem. Soc.* **1957**: 295.

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The yellow crystalline solids remaining after removal of 4,4′-dinitroazobenzene from bands (2) and (3) were found to be a mixture of *p*-nitro-*N*-methylaniline and *NN*′-dimethyl-4,4′-dinitro hydrazobenzene. Unchanged *p*-nitro-*N*-methylaniline was removed by sublimation at 100–130 °C/mm and the residue crystallized from carbon tetrachloride as yellow prisms, m.p. and mixed m.p. with an authentic sample of *NN*′-dimethyl-4,4′-dinitrohydrazobenzene, 175 °C (Found : C, 55·9 ; H, 4·6 ; N, 18·3% ; mol. wt., 331. Calc. for $C_{14}H_{14}N_4O_4$: C, 55·7 ; H, 4·6 ; N, 18·5% ; mol. wt., 302). The yield was 0·1 g (3%).

When 2 moles of iodosobenzene diacetate was used as the oxidant, *p*-nitroaniline (3% yield) and 4,4′-dinitroazobenzene (3% yield) were the only compounds isolated.

(ii) *Oxidation in Acetic Acid Solution.*—*p*-Nitro-*N*-methylaniline (3·8 g) in acetic acid (100 ml) was added to a solution of iodosobenzene diacetate (8·1 g ; 1 mole) in acetic acid (100 ml). After 4 days at room temperature, the acetic acid was distilled (20 mm) and the residue was extracted with hot benzene (insoluble material, 1–2 g). The benzene extract was chromatographed as described in Section II (*a*) (i). 4,4′-Dinitroazobenzene (3% yield) and *N*-nitroso-*N*-methyl-4-nitroaniline (18% yield) were obtained.

When 2 moles of oxidant was used, *p*-nitroaniline (9%), 4,4′-dinitroazobenzene (3%), and *N*-nitroso-*N*-methyl-4-nitroaniline (22%) were isolated.

NN′-dimethyl-4,4′-dinitrohydrazobenzene was not detected in either of these oxidations.

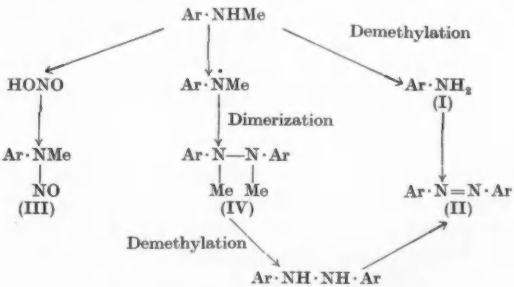
(*b*) *Oxidation of* NN-*Dimethylaniline*

NN-Dimethylaniline (1·8 g) was oxidized with iodosobenzene diacetate (14·5 g ; 3 moles) in benzene (600 ml). After 15 days, the deep red solution was filtered (insoluble material, 3·4 g) and chromatographed on alumina. Intractable tars were obtained by concentrating the various fractions but it was noted that a small amount of white solid was observed in the distillate obtained by concentrating the eluant. This was filtered and identified as *NNN*′*N*′-tetramethylbenzidine, m.p., and mixed m.p. with an authentic sample, 188 °C. It crystallized from methanol as prisms, m.p. 191 °C. The yield could not be determined owing to its volatility in benzene.

III. Discussion

(*a*) *Oxidation of* p-*Nitro*-N-*methylaniline*

(i) When *p*-nitro-*N*-methylaniline is oxidized in benzene and acetic acid solutions, it is seen that *p*-nitroaniline (I), 4,4′-dinitroazobenzene (II), *N*-nitroso-*N*-methyl-4-nitroaniline (III), and *NN*′-dimethyl-4,4′-dinitrohydrazobenzene (IV) are among the products formed. Possible mechanisms for the formation of these products are shown by



Ar=*p*-nitrophenyl

(ii) ***Formation of* N-*Nitroso*-N-*methyl-4-nitroaniline (III)*.**—It is obvious that rather deep-seated oxidation has taken place in all these reactions as only small

yields of isolable products have been obtained. Apparently one of the products is nitrous acid (or some similar compound) which reacts with unchanged *p*-nitro-*N*-methylaniline forming *N*-nitroso-*N*-methyl-4-nitroaniline.

(iii) *Formation of* NN'-*Dimethyl-4,4'-dinitrohydrazobenzene* (*IV*).—It has already been postulated (Pausacker 1953) that ArNH· radicals are produced as intermediates in the oxidation of primary aromatic amines with iodosobenzene diacetate. It is therefore reasonable to assume that the

radical would be formed during the oxidation of *p*-nitro-*N*-methylaniline and that part of this would dimerize forming *NN'*-dimethyl-4,4'-dinitrohydrazobenzene.

(iv) *Formation of* p-*Nitroaniline* (*I*).—*p*-Nitroaniline arises from demethylation of *p*-nitro-*N*-methylaniline and it has been frequently observed (cf. Horner and Schwenk 1949) that secondary amines may be demethylated by oxidizing agents. By analogy with Horner's mechanism for the demethylation of tertiary amines, the following mechanism is suggested :

$$Ar\ddot{N}HCH_3 + PhI(OAc)_2 \rightarrow Ar\dot{N}HCH_3^+ + OAc^- + Ph\dot{I}OAc$$

$$\downarrow$$

$$Ar\cdot NH\cdot\dot{C}H_2 + AcOH + Ph\dot{I}OAc \leftarrow Ar\cdot\dot{N}H\cdot\ddot{C}H_2 + AcOH + Ph\dot{I}OAc$$

$$\downarrow$$

$$Ar\cdot NH\cdot CH_2OAc + AcOH + Ph\cdot I$$

$$\downarrow H_2O$$

$$Ar\cdot NH_2 + CH_2O + 2AcOH + PhI$$

(v) *Formation of 4,4'-Dinitroazobenzene* (*II*).—As it has already been shown that *p*-nitroaniline can be oxidized to II by iodosobenzene diacetate in either benzene (Pausacker 1953) or acetic acid (Barlin, Pausacker, and Riggs 1954) solution, it may be assumed that II is formed via the oxidation of the *p*-nitroaniline resulting from the initial demethylation of the initial *p*-nitro-*N*-methylaniline. Alternatively, IV may be demethylated to form 4,4'-dinitrohydrazobenzene which would be readily oxidized to II.

It may be seen that there is a considerable difference in the products, dependent on whether the solvent is benzene or acetic acid. This has already been noted for other systems (Barlin, Pausacker, and Riggs 1954 ; Mitchell and Pausacker 1954 ; Pausacker and Scroggie 1954 ; Fox and Pausacker 1957).

(*b*) *Oxidation of* NN-*Dimethylaniline*

The only product was *NNN'N'*-tetramethylbenzidine (V), which was, however, only isolated in very small yield. It is presumed that the ion-radical ($Ph\dot{N}Me_2^+$) is involved as an intermediate in its formation (cf. Section III (*a*) (iv)),

and so demethylation could be a concurrent process. The low yield may therefore be attributable to the oxidation of the demethylation products to intractable mixtures as it has been found that *N*-methylaniline did not yield any identifiable compound under the same conditions. Naylor and Saunders (1950) have also isolated V from the oxidation of *NN*-dimethylaniline.

IV. References

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THE ALKALOIDS OF *CROTALARIA RETUSA* L.

By C. C. J. Culvenor* and L. W. Smith*

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Summary

In addition to monocrotaline, retronecine *N*-oxide and three new alkaloids, retusine, retusamine, and an incompletely characterized base, m.p. 130–132 °C, have been isolated from *Crotalaria retusa* L. The proportion of alkaloid occurring as *N*-oxide varied from 2 to 70 per cent. in different plant specimens. Hydrolysis of retusine gives 2,3,4-trimethyl-4-hydroxyglutaric acid 1,4-lactone (dihydroanhydromonocrotalic acid) and an amino alcohol, $C_8H_{15}O_2N$, probably hastanecine.

I. Introduction

Crotalaria species are common weeds in the northern parts of Australia and several have been suspected from time to time to be poison plants. Attention has recently been focused on *C. retusa* L. and this species has been confirmed by feeding experiments to be the major cause of a serious disease among station horses known as Kimberley horse disease (Rose *et al.* 1957*a*, 1957*b*). A feature of the disease is severe liver damage with megalocytosis of the liver cells, a characteristic effect of pyrrolizidine alkaloids (Bull 1955). There is some evidence that the disease can be produced by *Crotalaria* species other than *C. retusa* (Everist, personal communication) as might be expected from the general occurrence of alkaloids within the genus.

C. retusa was first recognized as a poison plant in the United States of America, where chemical investigation of the seed revealed large amounts of monocrotaline but no other alkaloid (Adams and Rogers 1939). The molecular structure of monocrotaline has been the subject of a lengthy series of papers by Adams and his co-workers, culminating in a proof of the cyclic diester structure I (Adams, Shafer, and Braun 1952). An examination of the vegetative parts of the plant has not been reported.

Assay of several samples of *C. retusa* from the Northern Territory and from the Kimberley region showed that monocrotaline was the predominant alkaloid in all parts of the plant, although in some samples a considerable proportion of it occurred as the *N*-oxide (see Table 1). The alkaloid content of the seed ranged as high as 5 per cent. Especially in vegetative material, but also in seed, paper chromatography revealed two other alkaloids as trace constituents. These have been isolated and one which is fully characterized has been named retusine.

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A sample of seed from the Barker and Lennard Rivers in the Kimberleys differed from all other samples in containing a substantial amount of a third new alkaloid, named retusamine. From this particular sample, retronecine *N*-oxide was also isolated. Structural studies on the new bases have been limited by the small amounts available. Their properties are listed in Table 2.

TABLE 1

ALKALOID ASSAYS OF CROTALARIA RETUSA L.

Plant Part	Origin	Alkaloid Content (% dry wt.)		R_F Values of *tert.*-Base
		tert.-Base	*N*-Oxide	
	Northern Territory			
Above ground parts	Alice Springs	1·4	0·1	0·30
Leaves	Katherine	1·6	0·5	0·30, 0·41, 0·48
Leaves+pods ..	Katherine	0·6	1·4	0·30, 0·42, 0·48
Seed	Katherine	5·0	0·1	0·30
	Western Australia			
Seed	Gogo Station, Kimberley	5·0	0·2	0·30
Seed	Barker and Lennard Rivers, Kimberley	1·4	0·9	0·30, 0·51

TABLE 2

PHYSICAL PROPERTIES OF NEW CROTALARIA RETUSA L. ALKALOIDS

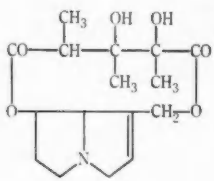
Alkaloid	Empirical Formula	Melting Point (°C)	Rotation $[\alpha]_D$ (deg)	R_F Values (in BuOH-AcOH)
Retusine	$C_{16}H_{25}O_5N$	174–175	+16 ($CHCl_3$)	0·46
Unnamed base ..	—	130–132	—	0·40
Retusamine ..	$C_{19}H_{25}O_7N$	169	+13 (EtOH)	0·52

II. STRUCTURE OF RETUSINE

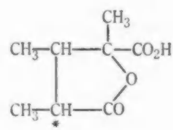
Retusine did not absorb hydrogen in the presence of Adams catalyst and was inert to dilute aqueous permanganate. Alkaline hydrolysis converted it into an amino alcohol, $C_8H_{15}O_2N$, and a mixture of acids which was separated on silica gel into two isomers, $C_8H_{12}O_4$, m.p. 130–131 °C, $[\alpha]_D^{20}$ +3·3° (ethanol) and m.p. 118 °C, $[\alpha]_D^{20}$ −60° (ethanol). These constants agree with those reported by Adams and Hauserman (1952) for epimeric 2,3,4-trimethyl-4-hydroxyglutaric acid 1,4-lactones (II) (named by these authors dihydroanhydromonocrotalic acids). For convenience, we designate the acid of m.p. 130 °C the α-acid and that of m.p. 118 °C the β-acid. The identity of the acids from retusine was established by direct comparison with authentic acids prepared from monocrotalic acid.

The isomeric acids differ in their configuration at the carbon atom indicated by an asterisk in II. Adams and Hauserman (1952) have shown that under suitable conditions interconversion proceeds to an equilibrium wherein the β-acid predominates. The α-acid is 65 per cent. epimerized by refluxing with 10 per cent. aqueous alkali for 11 hr, and completely epimerized by refluxing with concentrated hydrochloric acid for 11 days.

Hydrolysis of retusine with aqueous barium hydroxide at 100 °C, or with ethanolic sodium hydroxide at 50 °C, gave rise to the two acids at approximately equal rates but when hydrolysis was effected in 2N hydrochloric acid at 100 °C, only the α-acid was formed. It was confirmed that the β-acid is not changed by such mild acid conditions and it is therefore established that the configuration of retusine at the carbon atom in question is that of the α-acid.



(I)

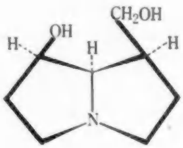


(II)

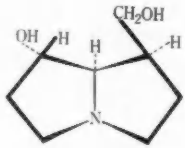
The amino alcohol has not been obtained in crystalline form but analysis of its hydrochloride, m.p. 116 °C, confirms the formula $C_8H_{15}O_2N$ which would be expected from the formulae of retusine and the esterifying acid. Its R_F value, 0·18 in butanol-acetic acid, is similar to those of other simple dihydroxypyrrolizidine derivatives. In view of the homogeneity of structure which generally obtains in this group of alkaloids, it is most likely that the amino alcohol is a 7-hydroxy-1-hydroxymethylpyrrolizidine (III).

Four isomeric amino alcohols, platynecine (Orekhov and Konovalova 1935), hastanecine (Konovalova and Menshikov 1945), turneforcidine (Menshikov, Denisova, and Massagetov 1952), and macronecine (Danilova, Utkin, and Massagetov 1955), have already been obtained by hydrolysis of alkaloids in this group, while a fifth, mikanecine (Manske 1936), was recently shown by Adams and Gianturco (1957) to be identical with platynecine. A sixth isomer, dihydroxyheliotridane, is known as a reduction product of heliotridine. The only compounds among these of known structure are platynecine (III*a*) and dihydroxyheliotridane (III*b*) (Adams and van Duuren 1954; Fodor 1954). Apart from mirror image compounds, only two more compounds of structure III are possible and some of the isomers in Table 3 must be identical with others or else be of different structure. The latter possibility is unattractive since the isomers are all saturated and thus necessarily bicyclic; a different structure would necessitate fused C_6–C_5, C_6–C_4, or C_7–C_4 rings, not previously observed in this field.

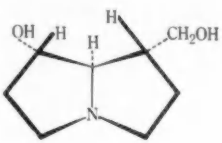
Warren (1955) has already pointed out the close similarity in properties of hastanecine and turneforcidine, peculiar in view of the reported depression in a mixed melting point (Menshikov, Denisova, and Massagetov 1952). Revising an earlier suggestion, but apparently without knowledge of the recently reported macronecine, Adams and Gianturco (1957) have now proposed that hastanecine and turneforcidine are the unknown diastereoisomers of structure III. Consideration of molecular rotation differences shows that this is most unlikely. Thus the difference in molecular rotations for the two undecided isomers should be approximately the same as for platynecine and dihydroxyheliotridane since both pairs differ only in configuration at C_7; for the latter pair the difference is



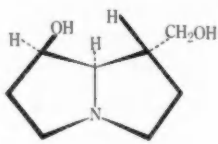
(IIIa)



(IIIb)



(IIIc)



(IIId)

78°, while for hastanecine and turneforcidine it is only 2°. The molecular rotation differences agree well, however, if diastereoisomer III*c* is macronecine, and diastereoisomer III*d* is hastanecine or turneforcidine. For we then have (considering hastanecine, all rotations in ethanol or methanol) $[M]_D$ III*b* $-[M]_D$ III*a* $=+78°$, $[M]_D$ III*c* $-[M]_D$ III*d* $=+91°$; and $[M]_D$ III*c* $-[M]_D$ III*b* $=+130°$, $[M]_D$ III*d* $-[M]_D$ III*a* $=+117°$. These suggestions for structures III*c* and III*d* are therefore probably correct. It also seems worthwhile to question here two published observations on the properties of hastanecine and turneforcidine, since if one or other were in error, these two compounds, and thus all isomers in Table 3, could have structure III. The possibilities are (i) turneforcidine is identical with hastanecine (contrary to the reported mixed melting point depression), or (ii) turneforcidine is enantiomeric with hastanecine (contrary to the reported signs of optical rotation). The base from retusine can also be identical or enantiomeric with the compound of structure III*d*.

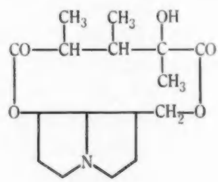
It therefore seems desirable that the properties of turneforcidine and hastanecine should be checked. To further clarify the situation, synthesis of the undecided diastereoisomers has been commenced.

TABLE 3

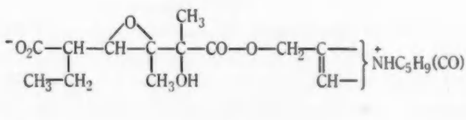
PROPERTIES OF COMPOUNDS $C_8H_{15}O_2N$ DERIVED FROM PYRROLIZIDINE ALKALOIDS

Compound	Melting Point (°C)	Optical Rotation (deg)		Hydrochloride Melting Point (°C)	References
		$[\alpha]_D$	$[M]_D$		
Platynecine ..	148–148·5	—84 (EtOH)	—131	—	Orekhov and Konovalova (1935)
Dihydroxyheliotridane	76–77	—34 (EtOH)	—53	—	Menshikov and Kurzokov (1949)
Hastanecine ..	113–114	— 9·1 (MeOH)	—14	(Hygroscopic)	Konovalov and Menshikov (1945)
Turneforcidine ..	118·5–120	—10·5 (MeOH)	—16	116	Menshikov, Denisova, and Massagetov (1952)
Macronecine ..	126–128	+49·4 (EtOH)	+77	152·3	Danilova, Utkin, and Massagetov (1955)
Base from retusine	—	—	—	116	

For the foregoing reasons, we consider retusine to be an ester derived from α-2,3,4-trimethyl-4-hydroxyglutaric acid 1,4-lactone (II) and a 7-hydroxy-1-hydroxymethylpyrrolizidine of structure III*d*. Evidence for a cyclic diester



(IV)



(V)

structure is provided by the infra-red absorption spectrum (taken in " Nujol ") which shows a carbonyl band at 1735 cm^{-1}, typical of an ordinary ester, and no band near 1780 cm^{-1} as would be required if the lactone ring of II were present

in retusine. The structure is therefore written as IV, this method of combining the dicarboxylic acid with the amino alcohol being preferred by analogy with monocrotaline.

III. Retusamine

The formula $C_{19}H_{25}O_7$ is tentatively assigned to retusamine although $C_{20}H_{27}O_7N$ cannot be excluded. In the presence of platinum catalyst, retusamine absorbs 2 moles of hydrogen to give a salt-like tetrahydro-derivative, which is hydrolysed by alkali (not immediately but on heating) to a dicarboxylic acid, $C_{10}H_{14}O_6$. On direct alkaline hydrolysis, retusamine gives an acid of similar physical properties but which slightly depresses the melting point of the former acid; insufficient was obtained for analysis. Both acids show only end-absorption in the ultraviolet. The basic product from these two experiments could not be characterized and appeared to be polymeric. Retusamine thus appears to be of the same type as the alkaloids otosenine and tomentosine which have been isolated from *Senecio othonnae* (Zhdanovich and Menshikov 1941) and *S. tomentosus* (Adams, Gianturco, and van Duuren 1956), respectively. These alkaloids are both of the formula $C_{19}H_{27}O_7N$, and on alkaline hydrolysis yield jaconecic acid, $C_{10}H_{16}O_6$, and what is apparently a polymerized amino alcohol. Insufficient retusamine is available to attempt isolation of the amino alcohol. Otonecine, which was isolated from otosenine after hydrolysis with hydrochloric acid, is regarded as an *N*-methylpyrroline containing a carbonyl group (Zhdanovich and Menshikov 1941).

Retusamine shows strong infra-red absorption at 1786 cm^{-1} (γ-lactone), 1745 and 1734 cm^{-1} (possibly 5-ring ketone and ester), and medium absorption at 1673 cm^{-1} (probably C=C). There are no absorption bands around 1612 cm^{-1} and 2400 cm^{-1}, the occurrence of which in the spectrum of tomentosine led Adams, Gianturco, and van Duuren (1956) to propose for this alkaloid an internal salt structure V. That retusamine is not an amino acid of this type is confirmed by its alkaline reaction to litmus and low solubility in dilute aqueous alkali. The behaviour of tomentosine in these tests was not reported. The presence of a γ-lactone ring in retusamine is of interest; the only other pyrrolizidine alkaloid in which it has been observed is grantianine (Adams and Gianturco 1956). The γ-lactone ring is also present in both of the acids derived from retusamine. The acid obtained by direct hydrolysis shows absorption bands at 1716, 1743, and 1762 cm^{-1} ("Nujol"), while that obtained after hydrogenolysis shows bands at 1718, 1741, 1762 cm^{-1} ("Nujol") and 1739, 1773 cm^{-1} (chloroform). The bands at 1718 and 1741 cm^{-1} are apparently due to dimeric and monomeric acid structures, respectively, the dimeric form disappearing in chloroform solution (cf. Flett 1951). Since the acid, $C_{10}H_{14}O_6$, obtained after hydrogenolysis, contains two free CO_2H groups (by titration) as well as the lactone ring, all O-atoms are accounted for. The number of H-atoms is consistent with no additional points of unsaturation. The formation of two different acids in the experiments described may be associated with epimerization of an asymmetric centre such as in the grouping, $R_1.CHR_2.CO_2R_3$. The acids are possibly related to the esterifying acid in grantianine, but structures will not be suggested until more evidence is available.

IV. Experimental

Microanalyses were made by the C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne. Melting points are corrected. The solvent used for paper chromatography was the upper phase resulting from shaking butanol with an equal volume of 5% acetic acid.

(*a*) *Total Alkaloid Assays.*—The method used was that of Culvenor and Smith (1955).

(*b*) *Isolation of Retusine and Base, m.p. 130–132 °C.*—The plant material was extracted with hot methanol, the methanol removed under reduced pressure, and the residue extracted with dil. HCl. If a substantial *N*-oxide content had been indicated for the particular sample by assay, the aqueous acid extract was reduced with zinc, more acid being added. Crude base was isolated by $CHCl_3$ extraction after making alkaline with excess ammonia. Crystallization from ethanol gave immediately large yields of monocrotaline, m.p. and mixed m.p. 201–202 °C (decomp.), $[\alpha]_D^{20}$—57° (*c*, 1·0 in $CHCl_3$) (Found: C, 59·4; H, 7·1; N, 4·2%. Calc. for $C_{16}H_{23}O_6N$: C, 59·1; H, 7·1; N, 4·3%).

The mother liquors from several batches were combined and evaporated and the residue was chromatographed on alumina. Although all the fractions obtained showed more than one spot, they yielded further crystalline material. For example, the fraction first eluted (14 g; R_F 0·47, 0·40, 0·33) gave monocrotaline (5 g), and a mixture (3·6 g; R_F 0·32, 0·46) mainly monocrotaline as the first 2 crops from ethanol. Further crystallization of the residue from ethanol and then from acetone gave pure *retusine*, R_F 0·46, as colourless needles, m.p. 174–175 °C, $[\alpha]_D^{20}$ +16·2° (*c*, 1·0 in $CHCl_3$) (Found: C, 61·9; H, 7·8; N, 4·6; O, 26·0%. Calc. for $C_{16}H_{25}O_5N$: C, 61·7; H, 8·1; N, 4·5; O, 25·7%).

When the final residues were chromatographed on alumina from benzene, the first eluate was an oil which deposited a small quantity of crystals. These were removed and recrystallized from acetone to give the second minor base as colourless plates, m.p. 130–132 °C, R_F 0·40. The pure material obtained was insufficient for analysis.

(*c*) *Isolation of Retusamine and Retronecine* N*-Oxide.*—A sample of seed (450 g), collected near the Barker-Lennard Rivers, W.A., was milled and extracted with hot methanol. The methanol was removed from the extract and the residue extracted with dil. HCl. The aqueous acid solution was divided into two equal portions and one was reduced with zinc and additional H_2SO_4. Both portions were made alkaline with ammonia and extracted separately with chloroform, to give crude "unreduced" and "reduced" alkaloid.

The crude unreduced and reduced alkaloid fractions were of similar composition and on crystallization from ethanol gave monocrotaline as prisms, m.p. and mixed m.p. 203 °C (decomp.) (Found: C, 59·1; H, 7·1; N, 4·4%. Calc. for $C_{16}H_{23}O_6N$: C, 59·1; H, 7·1; N, 4·3%). The methiodide had m.p. and mixed m.p. 205–206 °C (decomp.). The mother liquor was evaporated and portion of the residue submitted to chromatography on a column of kieselguhr moistened with phosphate buffer of pH 7·5. A small amount of a base, R_F 0·37, was eluted with light petroleum-carbon tetrachloride (4 : 1). Retusamine, R_F 0·45, the main component, was eluted with CCl_4, followed by monocrotaline which was eluted with $CHCl_3$-CCl_4 (3 : 2). The results indicated the following contents of individual constituents in the seed sample: monocrotaline, 1·19%; monocrotaline *N*-oxide, 0·87%; retusamine, 0·16%; retusamine *N*-oxide, 0·03%; base, R_F 0·37, 0·01%. The bulk of the retusamine was isolated from the crude alkaloid residue by chromatography on alumina from which it was eluted in a pure state by chloroform. Retusamine is readily soluble in ethanol, benzene, and hot water, fairly soluble in cold water. Recrystallization from a small volume of water and then from benzene-light petroleum gave long needles, m.p. 174·5 °C, $[\alpha]_D^{17}$ +13° (*c*, 1·93 in EtOH) (Found: C, 60·5; H, 6·7; N, 3·8; (C)Me, 2·8%. Calc. for $C_{19}H_{25}O_7N$: C, 60·2; H, 6·6; N, 3·7; Me, 4·0%. Calc. for $C_{20}H_{27}O_7N$: C, 61·1; H, 6·9; N, 3·6; Me, 3·8%).

The aqueous solution remaining after extraction of "unreduced" alkaloid was extracted with butanol which yielded on evaporation a dark brown gum. The ethanol-soluble portion of this was chromatographed on alumina from chloroform. Chloroform-50% ethanol eluted a crystalline solid (0·9 g), R_F 0·24 (strong), 0·18 (faint). The solid was readily soluble in water and alcohols, sparingly soluble in acetone. Recrystallization from acetone-methanol gave

needles or prisms, which decomposed before melting, usually becoming grey about 180 °C, black at 200 °C, but not collapsing to a liquid even at 220 °C. Occasionally, collapse to a black liquid occurred about 210 °C. The compound had $[\alpha]_D^{17}$ +41° (*c*, 4·24 in EtOH) (Found: C, 56·6; H, 7·6; N, 8·1%. Calc. for $C_8H_{13}O_3N$: C, 56·1; H, 7·7; N, 8·2%). It gave a red-brown colour on heating in acetic anhydride as is characteristic of *N*-oxides (Polonovski 1930). The empirical formula is that of retronecine *N*-oxide (isatinecine) which is reported as having m.p. 214–215 °C (decomp.), $[\alpha]_D$ +22·4° (water) (de Waal 1941; Leisegang and Warren 1949). Retronecine *N*-oxide was prepared in good yield by oxidation of retronecine with hydrogen peroxide (cf. Leisegang and Warren 1949) and formed prisms from acetone-methanol, R_F 0·24, darkening from 180–190 °C, charred by 215 °C without collapsing to a liquid (Found: C, 56·3; H, 7·8; N, 8·2%. Calc. for $C_8H_{13}O_3N$: C, 56·1; H, 7·7; N, 8·2%). A mixture with the compound from *C. retusa* behaved similarly on heating. The synthetic *N*-oxide had $[\alpha]_D^{17}$ +25° (*c*, 2·68 in water), $[\alpha]_D^{17}$ +42° (*c*, 3·34 in EtOH) thus confirming the identity of the *C. retusa* compound.

(*d*) *Monocrotaline* N-*Oxide*.—Monocrotaline (0·5 g) in ethanol (3 ml) was mixed with hydrogen peroxide (0·7 ml; 15%) and kept for 2 days before decomposing excess peroxide with manganese dioxide, filtering, and evaporating the filtrate *in vacuo*. The residue was dissolved in water and the solution washed with chloroform. The aqueous layer was re-evaporated and the residue crystallized from acetone-methanol to give *monocrotaline* N-*oxide* (0·41 g) as prisms, darkening at about 192 °C, and decomposing violently at about 196 °C (actual decomposition points are dependent on rate of heating) (Found: C, 55·0; H, 6·9%. Calc. for $C_{16}H_{23}O_7N.O.5H_2O$: C, 54·9; H, 6·9%). The sample analysed was dried 2 hr at 80 °C *in vacuo*; more rigorous drying caused decomposition. Monocrotaline *N*-oxide is insoluble in $CHCl_3$ and forms a crystalline picrate (from EtOH) which chars and decomposes at 165–175 °C. Reduction with zinc in 2N H_2SO_4 at room temperature gave monocrotaline in good yield; sulphur dioxide afforded only a poor yield of monocrotaline.

(*e*) *Alkaline Hydrolysis of Retusine*.—An aqueous solution of retusine (0·46 g) and barium hydroxide (1 g) was refluxed for 1 hr, cooled, saturated with carbon dioxide, and filtered. The filtrate was acidified to Congo red with HCl and extracted continuously with ether for 6 hr to give the acidic products as a colourless gum, R_F 0·71, 0·82, which later solidified. Recrystallization from ethyl acetate-light petroleum and from benzene gave α-2,3,4-trimethyl-4-hydroxyglutaric acid 1,4-lactone (70 mg), R_F 0·70, m.p. 130–131 °C, $[\alpha]_D^{20}$ +3·3° (*c*, 1·18 in EtOH) (Found: C, 56·8; H, 7·2; (C)Me, 24·0%; equiv. wt., 177. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 7·0; 3×Me, 26·1%; equiv. wt., 172). The mother liquors were evaporated and the residue (170 mg) chromatographed on silica gel (24 g) moistened with H_2SO_4 (0·5N; 16·5 ml). Chloroform eluted the acid of R_F 0·80 (61 mg), followed by mixed acids (37 mg), and then chloroform-2% acetone eluted the acid of R_F 0·70 (68 mg). The first fraction was recrystallized from ethyl acetate-light petroleum to give β-2,3,4-trimethyl-4-hydroxyglutaric acid 1,4-lactone as plates, m.p. 118 °C, $[\alpha]_D^{20}$ —60° (*c*, 0·5 in EtOH). The last fraction yielded more of the m.p. 130–131 °C isomer. Constants for the two acids are given by Adams and Hauserman (1952) as m.p. 132–134 °C, $[\alpha]_D$ +5·6°, and m.p. 117·5–119·5 °C, $[\alpha]_D$ —60°. Mixed melting points of the acids from retusine with the corresponding authentic acids, prepared as described below, were undepressed.

The residual aqueous solution from the hydrolysis of retusine was concentrated to a small volume, made alkaline with NaOH, and extracted with chloroform to give a basic oil (0·22 g), R_F 0·18. The base did not crystallize or form a crystalline picrate, and a picrolonate, m.p. 162–164 °C, which formed during a test could not be prepared on a larger scale. When vacuum distillation was attempted the base decomposed. It formed a crystalline hydrochloride which separated from ethanol-ether in needles, m.p. 116 °C, which were hygroscopic in humid weather but not in dry weather (Found: C, 49·6; H, 8·5; N, 6·6%. Calc. for $C_8H_{16}O_2NCl$: C, 49·6; H, 8·3; N, 7·2%).

(*f*) *Acid Hydrolysis of Retusine and Initial Formation of the α-Acid*.—To detect which acid somer was first formed, samples (*c*, 8 mg) of retusine were hydrolysed and the reaction mixture

spotted on paper at short intervals during the hydrolysis. With aqueous barium hydroxide at 100 °C, hydrolysis was complete in 3 min. Ethanolic sodium hydroxide at 50 °C gave a slower reaction but the acids were produced at about equal rates. Hydrolysis with 2N HCl at 100 °C was complete only after 6 hr and only the R_F 0·70 acid (α-acid) was formed. The R_F 0·80 acid was recovered unchanged after 3 hr boiling with 2N HCl.

(*g*) *Preparation of the Isomeric 2,3,4-Trimethyl-4-hydroxyglutaric Acid 1,4-Lactones from Monocrotalic Acid.*—Following the procedure of Adams and Hauserman (1952), methyl monocrotalate was dehydrated with phosphoric acid and the product hydrogenated in ether at 100 atm and 125 °C with Raney nickel as catalyst. The hydrogenation product was hydrolysed by refluxing with dilute NaOH for 4 hr and the solution acidified and extracted continuously with ether to give a mixture of acids, mostly R_F 0·70 and 0·80, but with a minor component of R_F 0·85. The main components were isolated by chromatography on silica gel and had m.p. 130–131 °C (Found : C, 56·1 ; H, 7·1%. Calc. for $C_8H_{12}O_4$: C, 55·8 ; H, 7·0%) and 117–118 °C (Found : C, 55·5 ; H, 6·5%) respectively. The latter was difficult to separate from the third acid which may be a diastereoisomer.

(*h*) *Hydrogenation of Retusamine.*—The base (100 mg) was reduced in ethanol (10 ml) in the presence of platinum oxide catalyst and absorbed 2 moles of hydrogen (a quantitative experiment on 15·0 mg retusamine gave absorption of 1·94 ml hydrogen ; calc. for 2 moles, 1·90 ml). After removing the catalyst, the solution was evaporated to give a gum which crystallized from acetone. The total residue was dissolved in 2N H_2SO_4 and extracted with $CHCl_3$ to give a gum (6·8 mg), R_F 0·74, 0·85. The solution was made alkaline to phenolphthalein and extracted with $CHCl_3$ to give a gum (5·0 mg), R_F 0·21, 0·30. The very small amount obtained in this way conforms with the view that the reduction product is an amino acid rather than a salt of separately ionized acidic and basic entities. The residual aqueous solution was made alkaline again with NaOH and heated at 100 °C for 2 hr with nitrogen bubbling through the solution and then into a dinitrophenylhydrazine trap. No carbonyl compound was evolved. After the hydrolysis, extraction with $CHCl_3$ gave an oily base (35 mg), R_F 0·23, 0·41, of peculiar odour and yielding no crystalline derivatives. The aqueous solution was acidified and extracted with $CHCl_3$ to give an acid gum (35 mg), R_F 0·72, 0·85, which yielded crystals from benzene-acetone. Recrystallization from this solvent gave an *acid* of R_F 0·74 as needles, m.p. 181 °C (decomp.) (Found : C, 52·7 ; H, 6·0% ; equiv. wt., 119. Calc. for $C_{10}H_{14}O_6$: C, 52·2 ; H, 6·1% ; equiv. wt. (for $2CO_2H$), 115). A mixture with jaconecic acid melted at 155–157 °C.

(*i*) *Hydrolysis of Retusamine.*—When retusamine (100 mg) was heated in 1N NaOH (10 ml) at 100 °C under nitrogen, no volatile carbonyl compound was removed in the nitrogen but the solution rapidly changed to a reddish black colour. After 2 hr, the solution was concentrated *in vacuo* to 5 ml ; the distillate gave no precipitate with dinitrophenylhydrazine and had no odour. The residual solution was acidified and extracted continuously with chloroform to give a gum (52 mg), R_F 0·76 (strong), 0·85 (weak), which after two crystallizations from benzene-acetone gave needles, R_F 0·74, m.p. 178 °C (decomp.), in insufficient quantity for analysis. A mixture with the acid from the hydrogenation experiment melted at 172 °C, and a mixture with jaconecic acid at 155–156 °C.

The residual aqueous solution was made alkaline, evaporated to dryness *in vacuo*, and the residue extracted with ethanol. The extract was evaporated and the product again taken up in ethanol, filtered, and recovered from solution. The brown, resinous base (65 mg) had R_F 0·03, 0·10, 0·17, and was largely insoluble in acetone even on refluxing, and gave an amorphous precipitate with picric acid.

V. Acknowledgments

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THE ALKALOIDS OF *CROTALARIA SPECTABILIS* ROTH.

By C. C. J. Culvenor* and L. W. Smith*

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Summary

Monocrotaline and a new alkaloid, spectabiline, are isolated from *Crotalaria spectabilis* Roth. in nearly equal amounts. Spectabiline is shown to be an *O*-acetylmonocrotaline and has been prepared by acetylation of monocrotaline.

I. Introduction

Widely grown in the U.S.A. as a cover crop, *Crotalaria spectabilis* Roth. has been found there to be toxic to animals (Becker *et al.* 1935; Piercy and Rusoff 1946). Chemical examination of the seed revealed a high content of monocrotaline which was the only alkaloid present in detectable amount (Neal, Rusoff, and Ahmann 1935; Adams and Rogers 1939). The botanical affinity with *C. retusa* L., whose seed is also rich in monocrotaline (Adams and Rogers 1939; Culvenor and Smith 1957), is very close, both being in the same subsection of the genus. *C. spectabilis* is now naturalized as a weed in Queensland and in order to confirm the presence of monocrotaline, material† from this source has been examined.

Preliminary assays showed a very high alkaloid content (5·8 per cent.) in the seed but considerably less (0·63 per cent.) in the whole plant. Results are given in Table 1. Two alkaloids, R_F 0·30 and 0·43, were present in almost equal amount. Both occurred to a small extent in the seed, but in large proportion in the whole plant, as the *N*-oxide. The alkaloid of R_F 0·30 is monocrotaline; the other is new and has been named spectabiline.

II. Structure of Spectabiline

Spectabiline has the empirical formula $C_{18}H_{25}O_7N$. Alkaline hydrolysis gave retronecine and an oily acid mixture, while acid hydrolysis gave rise to monocrotalic acid or monocrotaline depending on the conditions. The nature of the carbon skeleton was thus established and it appeared likely that spectabiline is an acetyl derivative of monocrotaline. Isolation of acetic acid from the hydrolysis products was not achieved but microanalysis provided evidence for an acetyl group. The determination of *O*-acetyl employs alkaline hydrolysis and there appeared to be a danger of decomposition products such as monocrotic acid affecting the result. However, a " blank " determination on monocrotaline showed 0·3 mol "*O*-acetyl" whereas spectabiline showed 1·3 mol. Similarly, 2·6 mol *C*-methyl was found for monocrotaline and 3·4 mol for spectabiline.

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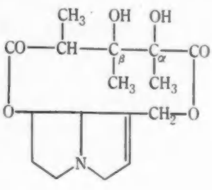
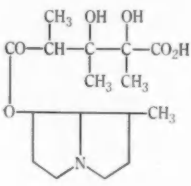
† A herbarium voucher, No. LJW. 1578, is deposited in the Australian Herbarium, C.S.I.R.O., Canberra.

The products obtained from hydrogenation of spectabiline depend on the conditions during isolation. Experiments in which the basic product was isolated first gave retronecanol and anhydromonocrotalic acid. When the reduction was effected in very dilute aqueous sulphuric acid, the product was an amino acid since no acid was obtained by immediate extraction of the reaction solution ; after basification, retronecanol and subsequently anhydromonocrotalic acid could be isolated. At the time, this suggested that the acetyl group may be on the α-OH group of monocrotaline (I). Thus hydrogenation of monocrotaline had given only retronecanol and monocrotalic acid and it was thought that attack by the α-OH group on the second ester linkage caused immediate decomposition of the initially formed amino acid (II). Stability of the amino acid from



(I)



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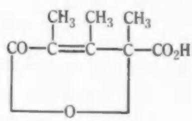

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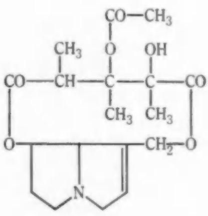
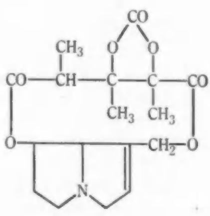


(IV)



(V)

spectabiline therefore indicated absence of a free α-OH group. However, it was found that monocrotaline also yields a stable amino acid under similar conditions, as has since been reported by Adams and Gianturco (1956). Subsequently, the esterifying acid of spectabiline—acetylmonocrotalic acid—was isolated intact by decomposing the initially formed amino acid with 2N sulphuric acid. The acid so obtained was identical with that prepared by acetylation of monocrotalic acid.

The isolation of anhydromonocrotalic acid (III) from spectabiline after hydrogenolysis is surprising since the elements of acetic acid are lost under very mild conditions. Since formation of III from monocrotaline under comparable conditions has not been observed, its isolation from spectabiline implies attachment of the acetyl group at the β-position. The isolation of acetylmonocrotalic acid provides firm evidence that the α-OH group is available for lactone formation

without loss of the acetyl group from the molecule. Migration of the acetyl group to the adjacent hydroxyl under the conditions used is most unlikely; transformation of spectabiline itself in this way has not been observed. Structure IV can therefore be written for spectabiline.

Conversion of monocrotaline into spectabiline has been accomplished with acetyl chloride and with ketene. The former reagent gave spectabiline and diacetylmonocrotaline while ketene gave spectabiline and an acetyl-free compound, $C_{17}H_{21}O_7N$. The compound $C_{17}H_{21}O_7N$ is reconverted to monocrotaline by refluxing with hydrochloric acid and may be the cyclic carbonate (V). Attempts to prepare it from monocrotaline and phosgene failed. Diacetylmonocrotaline also gave monocrotaline on acid hydrolysis thus demonstrating retention of the cyclic diester structure.

Unexpectedly, it has not been found possible to convert acetylmonocrotalic acid into anhydromonocrotalic acid. Acid hydrolysis gave monocrotalic acid while under alkaline conditions the product appeared to be monocrotic acid. It is apparent therefore that loss of acetic acid to give an olefine occurs only with the amino acid which is the initial hydrogenolysis product. Under appropriate conditions, both anhydromonocrotalic acid and acetylmonocrotalic acid were also obtained from the hydrogenolysis of diacetylmonocrotaline. Here the ready removal of the acetyl group from the α-OH group is also noteworthy.

III. Experimental

Microanalyses were made by the C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne. Melting points are corrected. The solvent used for paper chromatography was the upper phase resulting from shaking butanol with an equal volume of 5% acetic acid.

(*a*) *Preliminary Assays.*—The assay method used was that of Culvenor and Smith (1955).

(*b*) *Isolation of the Alkaloids.*—The milled plant material was extracted with hot methanol, the methanol distilled from the extract, and the residue extracted with dil. H_2SO_4. The extract from whole plant, but not that from seed, was reduced with zinc dust and additional H_2SO_4. The crude alkaloid was obtained by making the solution alkaline to phenolphthalein with NH_3 and extracting with $CHCl_3$. Seeds (740 g), pods plus immature seed (1900 g), and whole plant (1710 g) gave crude base (53, 25, and 9 g, respectively), R_F 0·30, 0·44.

Recrystallization of the crude base from ethanol gave essentially pure monocrotaline. Recrystallization gave colourless prisms, m.p. and mixed m.p. 202–203 °C, $[\alpha]_D^{20}$ —55° (*c*, 1·0 in ethanol) (Found: C, 59·0; H, 7·2; N, 4·2%. Calc. for $C_{16}H_{23}O_6N$: C, 59·1; H, 7·1; N, 4·3%).

The crude base mother liquors were evaporated and the residue crystallized from a small volume of acetone-light petroleum. The product was recrystallized twice from ethanol to give colourless prisms of spectabiline, m.p. 185·5–186 °C, R_F 0·43, $[\alpha]_D^{20}$ +121° (*c*, 1·7 in chloroform), $[\alpha]_D^{20}$ +143° (*c*, 1·38 in ethanol) (Found: C, 59·1; H, 6·9; N, 3·4; O, 30·2; *O*-acetyl, 14·9; *C*-methyl, 14·1%; equiv. wt., 367. Calc. for $C_{18}H_{25}O_7N$: C, 58·9; H, 6·8; N, 3·7; O, 30·5; 1×$COCH_3$, 11·7; 4×CH_3, 16·4%; equiv. wt., 367).

The final gummy residues were purified by countercurrent distribution between $CHCl_3$ and dil. HCl. After seven transfers with 25 ml of each phase, a brown gum (6·8 g) gave no base in tube 1, mainly monocrotaline (2·0 g) in tube 2, and mainly spectabiline (3·4 g) in tubes 3–5.

(*c*) *Alkaline Hydrolysis of Spectabiline.*—Spectabiline (1·0 g) was refluxed with $Ba(OH)_2$ (2 g) in water (25 ml) for 2 hr. The mixture was cooled, saturated with CO_2, filtered, and the filtrate acidified with HCl. Continuous ether extraction of the acid solution for 6 hr gave a brown liquid (0·35 g), partly volatile at 70–80 °C/0·8 mm. The distillate was acidic but had an

equiv. wt. of 750 and presumably contained much non-acidic material. The residual aqueous solution was evaporated, the residue extracted with ethanol, and the ethanolic extracts concentrated to give large prisms of retronecine hydrochloride, m.p. and mixed m.p. 164–165 °C.

(*d*) *Acid Hydrolysis of Spectabiline.*—(i) Spectabiline (0·5 g) and HCl (10%; 15 ml) were refluxed for 6 hr, and the mixture cooled and extracted continuously with ether. The product (0·23 g, m.p. 174–176 °C) was crystallized from acetone-light petroleum to give monocrotalic acid, m.p. and mixed m.p. 182–183 °C, R_F 0·54, $[\alpha]_D^{26}$ —2·6° (*c*, 1·92 in ethanol) (Found: C, 51·5; H, 6·5%; equiv. wt., 187. Calc. for $C_8H_{12}O_5$: C, 51·5; H, 6·4%; equiv. wt., 188).

(ii) Spectabiline (1·2 g) was refluxed with HCl (10%; 15 ml) for 4 hr, and the mixture cooled and extracted with ether to give monocrotalic acid (0·43 g), R_F 0·55. The aqueous solution was then evaporated to a small volume, basified, and extracted with $CHCl_3$ to give a solid (0·35 g), R_F 0·30. Crystallization from ethanol gave monocrotaline, m.p. and mixed m.p. 204–205 °C. An attempt to detect acetic acid in the original hydrolysis solution failed.

(*e*) *Hydrogenation of Spectabiline.*—(i) When spectabiline (0·5 g) was shaken with hydrogen and reduced platinum oxide in ethanol containing a little acetic acid, hydrogen (2·0 moles) was absorbed. The mixture was filtered and evaporated to dryness, and the residue taken up in aqueous NaOH and extracted with $CHCl_3$ to give a gummy base (0·23 g), R_F 0·38. The base distilled from a bulb tube at 60–100 °C/0·4 mm giving retronecanol, m.p. and mixed m.p. 93–94 °C (Found: C, 67·7; H, 10·6; N, 9·8%. Calc. for $C_8H_{15}ON$: C, 68·1; H, 10·6; N, 9·9%). The residual aqueous solution was acidified and extracted continuously with ether to give an oily acid (0·35 g), R_F 0·70. This acid was purified by washing a solution in aqueous alkali with ether, recovered and crystallized from ethyl acetate-light petroleum, when it formed colourless plates, m.p. 117–118 °C, R_F 0·70, $[\alpha]_D^{20}$ +214° (*c*, 1·19 in ethanol) (Found: C, 56·5; H, 6·1%; equiv. wt., 165. Calc. for $C_8H_{10}O_4$: C, 56·4; H, 5·9%; equiv. wt., 170). The physical constants correspond with those of anhydromonocrotalic acid, and a mixture with an authentic specimen (see below) melted undepressed.

(ii) Spectabiline (0·5 g) was hydrogenated in very dil. H_2SO_4. Hydrogen (2 moles) was absorbed, and after removing the catalyst the solution was extracted continuously with ether. No acid was obtained in the ether. The solution was brought to pH 7, extracted with $CHCl_3$ which again gave no product, and then with butanol. The butanol extract was evaporated without heating above 50 °C. The residue could not be made to crystallize; it showed an elongated spot on a paper chromatogram with both acid and base reacting portions. Monocrotaline, hydrogenated and worked up under the same conditions, gave closely similar results.

(iii) Spectabiline (0·5 g) was hydrogenated in ethanol with Raney nickel catalyst; 2 moles of hydrogen was absorbed. The catalyst was removed, the filtrate evaporated, and the resulting gum taken up in dil. H_2SO_4. Ether extraction of this solution gave a gummy acid (0·29 g), R_F 0·73, which yielded a brucine salt, m.p. 184 °C, undepressed on admixture with the brucine salt of acetylmonocrotalic acid (preparation described below) (Found: C, 63·4; H, 6·2; N, 4·8%. Calc. for $C_{33}H_{40}O_{10}N_2$: C, 63·5; H, 6·4; N, 4·5%).

(*f*) *Anhydromonocrotalic Acid.*—The method of preparation of Adams and Wilkinson (1943) was followed. Monocrotalic acid (1·0 g) was refluxed in thionyl chloride (20 ml) for 5 hr and the mixture twice evaporated from ether in a stream of air. After drying overnight in a desiccator, the residue was a gum (1·53 g), R_F 0·75, 0·25. This was chromatographed on a column of silica gel (24 g) moistened with sulphuric acid (0·5N; 16·5 ml). Benzene eluted non-acidic material (0·5 g) and chloroform-benzene (3 : 1) eluted an acid, R_F 0·75, which crystallized from benzene in plates or prisms, m.p. 117–118 °C, $[\alpha]_D^{20}$ +219° (*c*, 1·02 in ethanol) (Found: C, 56·6; H, 6·0%. Calc. for $C_8H_{10}O_4$: C, 56·4; H, 5·9%). For anhydromonocrotalic acid, Adams and Wilkinson quote m.p. 115–117 °C, $[\alpha]_D^{28}$ +196° (*c*, 2·79 in ethanol).

(*g*) *Reaction of Monocrotaline with Ketene.*—Ketene was passed into a solution of monocrotaline (1 g) in chloroform for 1 hr. The product from six such runs, showing spots of R_F 0·29 (weak), 0·40, 0·50, and 0·65, was chromatographed on alumina. Benzene-light petroleum eluted a non-basic liquid (1·7 g), probably ketene dimer, followed by a liquid (4·5 g) of similar nature but which deposited crystals of R_F 0·47, 0·65. Benzene eluted base (4·4 g), R_F 0·40, 0·50, 0·65,

and benzene-chloroform eluted further base (3·7 g), R_F 0·40, 0·50 (weak). Further chromatography produced the bases of R_F 0·40, 0·50 in a pure state; the former crystallized from acetone-light petroleum in hexagonal prisms, m.p. 182–183 °C, mixed m.p. with spectabiline, 186 °C, $[\alpha]_D^{20}$ +132° (*c*, 0·3 in ethanol). The base, R_F 0·50, was crystallized from benzene-light petroleum and finally from ethanol to give fine needles, m.p. 213 °C, $[\alpha]_D^{20}$ +78·5 (*c*, 0·84 in ethanol) (Found: C, 58·5; H, 6·3; O, 31·4; N, 4·1%; equiv. wt., 362. Calc. for $C_{17}H_{21}O_7N$: C, 58·1; H, 6·0; O, 31·9; N, 4·0%; equiv. wt., 351). This compound, possibly monocrotaline carbonate (V), shows only general absorption in the ultraviolet region.

(*h*) *Acid Hydrolysis of the Base, $C_{17}H_{21}O_7N$.*—The base (0·8 g) was refluxed in 10% HCl for 3 hr. The mixture was cooled and extracted continuously with ether to give an acid (0·04 g), R_F 0·55. The aqueous reaction solution was made alkaline with sodium carbonate and extracted with $CHCl_3$ to give base (0·32 g), R_F 0·30 (main spot), 0·48. Chromatography on alumina gave unchanged starting material, feathery needles from light petroleum, m.p. 206–207 °C, and monocrotaline, prisms from ethanol, m.p. and mixed m.p. 199–200 °C.

TABLE 1

ALKALOID CONTENT OF CROTALARIA SPECTABILIS ROTH.

Plant Part	*tert.*-Base (%)	Base *N*-Oxide (%)	Base R_F Values (in BuOH-AcOH)
Seed ..	5·4	0·4	0·30, 0·44
Pod ..	0·4	0·18	0·30, 0·44
Whole plant	0·17	0·46	0·30, 0·44

(*i*) *Acetylation of Monocrotaline with Acetyl Chloride.*—(i) Monocrotaline (1·0 g) was refluxed for 3 hr with acetyl chloride (15 ml) and excess of the latter evaporated. The product was taken up in dilute acid, and the solution made alkaline and extracted with $CHCl_3$ to give a gum (1·37 g), R_F 0·28 (weak), 0·40, 0·60. When this was chromatographed on alumina, the last component, R_F 0·60 (0·74 g) was eluted by benzene-light petroleum, while the other two were eluted later as mixtures only. The base of R_F 0·60, diacetylmonocrotaline, crystallized from light petroleum in large prisms, m.p. 101 °C, $[\alpha]_D^{20}$ +152° (*c*, 2·56 in ethanol) (Found: C, 58·9; H, 6·6; N, 3·4; O, 30·7; *O*-acetyl, 22·6%; equiv. wt., 420. Calc. for $C_{20}H_{27}O_8N$: C, 58·7; H, 6·6; N, 3·4; O, 31·3; 2×$COCH_3$, 21·0%; equiv. wt., 409).

(ii) Finely ground monocrotaline (6 g) was refluxed with acetyl chloride (20 ml) for 30 min. The base partly dissolved and then a hydrochloride separated. The precipitate was filtered off and the filtrate evaporated. Both the precipitate and the residue from the filtrate had R_F 0·40, 0·56, and they were combined and taken up in dil. HCl. This solution was washed with $CHCl_3$, which removed a gum (2·1 g), R_F 0·38, 0·51. The residual aqueous solution was basified and extracted with $CHCl_3$, and the resulting base (3·2 g) was crystallized from ethanol to give spectabiline (1·25 g) as colourless prisms, m.p. and mixed m.p. 185–186 °C, $[\alpha]_D^{20}$ +140° (*c*, 1·17 in ethanol) (Found: C, 58·8; H, 6·9; *O*-acetyl, 13·9%; equiv. wt., 364. Calc. for $C_{18}H_{25}O_7N$: C, 58·8; H, 6·8; 1×$COCH_3$, 11·7%; equiv. wt., 367).

(*j*) *Acid Hydrolysis of Diacetylmonocrotaline.*—The diacetyl compound (0·7 g) was refluxed for 2 hr in 10% HCl. The solution was cooled and extracted with ether to give an acid gum (0·2 g), R_F 0·60, smelling strongly of acetic acid. The residual aqueous solution was basified and extracted with $CHCl_3$ to give a crystalline base (0·21 g), R_F 0·14, 0·27, which from ethanol yielded colourless prisms of monocrotaline, m.p. and mixed m.p. 204 °C. Under more vigorous conditions (20% HCl for 5 hr), the products were monocrotalic acid and retronecine.

IV. ACKNOWLEDGMENTS

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THE CHEMICAL CONSTITUENTS OF AUSTRALIAN *FLINDERSIA* SPECIES

X. THE CONSTITUENTS OF F. DISSOSPERMA (F. MUELL.) DOMIN AND ITS RELATIONSHIP TO F. MACULOSA (LINDL.) F. MUELL.

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Summary

The constituents of the leaves, bark, and wood of *Flindersia dissosperma* (F. Muell.) Domin and of the wood of *F. maculosa* (Lindl.) F. Muell., have been isolated and identified. The chemical evidence supports the view that these two species and *F. collina* F.M. Bail. are closely related.

I. INTRODUCTION

Considering only the Australian species of *Flindersia*, it can be stated that *F. maculosa* (Lindl.) F. Muell. is unique for two reasons. Firstly, it has simple leaves, and secondly, it withstands more arid conditions than any of its congeners. If it is assumed that *F. australis* R.Br., with pinnate leaves and inhabiting higher rainfall areas, is primitive because it has a full complement of stamens (no staminodes), alternate leaves, and a capsule which does not break up into free valves, then it might be argued that *F. maculosa* is an aberrant species which has undergone leaf reduction and become adapted to dry conditions, perhaps in response to the stimulus of a prolonged period of increasing aridity.

If one looks for species showing characters intermediate between those of *F. maculosa* and more typical members of the genus, two species, *F. dissosperma* (F. Muell.) Domin and *F. collina* F. M. Bail., immediately stand out. The leaves of both show a step towards the simple-leaved state by having rather broad wings on the petiole and rhachis (when present), and sessile leaflets. Further, both approach *F. maculosa* in having rather small, similarly ornamented capsules, and they occupy areas with slightly lower rainfall than do most members of the genus. *F. dissosperma* is closer to *F. maculosa*, because it has 3(–5) leaflets and only very slightly larger capsules, while *F. collina* has 5(–7) leaflets and distinctly larger capsules.

It is interesting to note that some earlier botanists have treated *F. maculosa* and *F. dissosperma* as a single variable species, possibly because of the similarity of the capsules, and *F. collina* as a variety of *F. dissosperma*.

The botanical relationships between the three species are reflected in their chemical constituents, so far as they are known. The bark of *F. collina* contains

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collinin (Anet, Blanks, and Hughes 1949), kokusaginine and flindersiamine (Anet *et al.* 1952), and hesperidin (unpublished observation), but the leaves and the wood have not yet been investigated. *F. maculosa* is a rather variable species. One sample of leaves gave collinol, kokusaginine, maculosidine, and flindulatin and the bark gave collinol, kokusaginine, maculosine, maculine, and flindissol. A second sample of leaves contained flindulatin and only traces of alkaloids, and the bark only traces of alkaloids. A third sample of leaves again yielded flindulatin and traces of alkaloids but from the bark was obtained collinin, kokusaginine, maculine, and flindersiamine (Brown *et al.* 1954). An examination of a large quantity of the wood has now revealed the presence of dictamnine and maculine as the chief alkaloids, together with trace amounts of flindersiamine, kokusaginine, skimmianine, and maculosine. *F. dissosperma* also has now been found to be a variable species. One sample of bark yielded flindersiamine and flindissol but a second sample gave collinol, maculine, and flindissol. The leaves of the first sample afforded skimmianine, flindersiamine, and flindissol and a small wood sample corresponding to the second bark sample gave dictamnine.

Owing to the difficulty of isolating small amounts of phenolic substances from leaves there may possibly be little significance in the isolation of flindulatin from *F. maculosa* leaves and not from *F. dissosperma* leaves, but the other results are surely significant. Hesperidin, which is readily isolated and identified, is absent from the barks of *F. maculosa* and *F. dissosperma* but is present in *F. collina* bark and also in the barks of many other members of the genus (unpublished data). Collinol is probably an artefact derived from the readily degraded collinin which may therefore be considered to be present in all three species. The triterpene, flindissol, which is readily isolated, is absent from *F. collina* bark but is present in the barks from the other two species. The alkaloidal constituents of the three species are clearly very similar but *F. maculosa* contains the greatest variety, at least of those alkaloids occurring in more than trace amounts. It is of interest to note that the chief wood alkaloids present a simpler hydroxylation pattern than the bark or the leaf alkaloids.

II. Experimental

Melting points are uncorrected. The analyses were carried out by Dr. K. W. Zimmermann of the C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne, and by Miss B. Stevenson, University of Sydney. Light petroleum refers to the fraction of b.p. 60–90 °C.

(*a*) *Isolation of Hesperidin from* F. collina.—The ground bark (1·8 kg) was exhausted with warm light petroleum in a continuous extractor to remove alkaloids and collinin, and then with acetone. The acetone extract was concentrated to about 1000 ml, cooled, and filtered. The residue, after washing with acetone and methanol, was almost pure hesperidin (0·5 g). It crystallized from methanol in small colourless needles, m.p. and mixed m.p. 256–257 °C (decomp.). The acetate crystallized from methanol as colourless microscopic needles, m.p. and mixed m.p. 175–176 °C. The aglycone separated from aqueous ethanol in colourless needles, m.p. and mixed m.p. 226–227 °C (decomp.).

(*b*) *Extraction of* F. maculosa *Wood.*—The coarsely shredded wood (57 kg) was extracted at room temperature with light petroleum (b.p. 90–110 °C) three times, with acetone three times, and with methanol three times. The extracts were concentrated and then worked up separately.

(i) The light petroleum extract (1250 ml) after keeping for several weeks deposited a dark green viscous oil. The supernatant liquid was decanted and extracted repeatedly with warm 5%

HCl (1800 ml). The acid extract was combined with a similar extract of the green oil and the cloudy solution washed with ethyl acetate (3×200 ml). Basification and extraction with chloroform then yielded a yellowish brown partly crystalline solid (7·3 g) which was partially purified by passing its chloroform solution through a short column of alumina. The crude material thus obtained was yellow and completely crystalline (7·0 g).

The ethyl acetate washings were extracted with 5% HCl (4×100 ml), the extract basified, and the liberated bases shaken out with chloroform. The brown residue (0·29 g) obtained from the chloroform extract was chromatographed in benzene on alumina. Evaporation of the benzene eluates and crystallization of the residue from methanol yielded colourless prisms (19 mg), m.p. 130–132 °C, undepressed by admixture with authentic dictamnine (m.p. 131–132 °C).

The main bulk of the alkaloidal material (7·0 g) was dissolved in benzene and chromatographed on alumina (3·25 by 29 cm). Using increasing proportions of ether according to the procedure of Iriarte *et al.* (1956) 50 fractions of approximately 100 ml were collected. The column was finally stripped with chloroform (1000 ml) and with methanol (900 ml) but nothing crystalline could be obtained from these eluates. The residues with similar melting ranges from the other eluates were combined, recrystallized, and chromatographed again if necessary. The yields of the individual alkaloids, which were identified by mixed m.p. and colour tests, are given in the order of their emergence from the column: dictamnine (3·34 g), m.p. 131–132 °C; maculine (1·12 g), m.p. 194–196 °C; kokusaginine (10 mg), m.p. 167–168 °C; flindersiamine (35 mg), m.p. 207–208 °C; and skimmianine (3 mg), m.p. 174–177 °C. The light petroleum extract from which the alkaloids had been removed yielded no pure substances.

(ii) The acetone extract was diluted with water and the mixture exhausted with chloroform. The extract was evaporated and the residue extracted repeatedly with warm 5% HCl. The liberated bases (10·65 g) which formed a thick brown oil were chromatographed as above, but only dictamnine (0·4 g) and maculine (0·2 g) could be isolated.

(iii) The methanol extract, processed as in (ii), gave a crude alkaloid fraction as a dark brown solid (1·67 g) from which dictamnine (0·15 g) and maculosine (3 mg), m.p. and mixed m.p. with an authentic specimen, 226–227 °C, were isolated.

(c) *Extraction of* F. dissosperma *Leaves*.—The milled leaves (3·6 kg) were extracted in a continuous extractor with light petroleum and then methanol, the extracts being worked up separately.

The light petroleum extract was concentrated to a small bulk and kept when a yellow crystalline precipitate gradually formed. By fractional crystallization from benzene it was separated into a less soluble and a more soluble component. The latter, after repeated recrystallization from benzene-light petroleum, was identified as flindissol (1·2 g) and showed the characteristic double m.p. 137 and 198 °C, unchanged by admixture with authentic material (Found: C, 79·4; H, 9·9%. Calc. for $C_{30}H_{46}O_3$: C, 79·5; H, 9·9%).

The less soluble substance (0·6 g) crystallized from ethanol in colourless prisms, m.p. 207–208 °C, undepressed by admixture with flindersiamine. The picrate, broad yellow needles, m.p. 200–202 °C, undepressed by flindersiamine picrate, and the *iso*-compound, colourless needles, m.p. 209 °C, undepressed by *iso*flindersiamine, were also prepared.

The light petroleum mother liquors were evaporated to dryness and the residue repeatedly extracted with warm 5% HCl. The crude alkaloids liberated by ammonia were extracted with ether, the solution dried, and evaporated. A solution of the brown crystalline residue in benzene was passed through a short column of alumina to remove colouring matters and the product recovered. Crystallization from methanol gave colourless prisms (0·8 g), m.p. 186 °C, not raised by further recrystallization. By direct comparison it was shown to be identical with "bourjotine" and was separated into flindersiamine and skimmianine by chromatography (Cannon *et al.* 1952).

The methanol extract on working up in the usual way gave a crude alkaloid fraction which on chromatography in benzene on alumina afforded more flindersiamine (0·4 g).

(d) *Extraction of* F. dissosperma *Bark*.—(i) The ground bark (4·2 kg) was extracted in a continuous extractor with light petroleum and then methanol.

On concentration and keeping, the light petroleum extract gave crude flindissol (32 g), and from the mother liquors flindersiamine (0·3 g) was isolated by the usual method, but no other substance could be obtained.

The methanol extract yielded no hesperidin but a small amount of flindersiamine (0·08 g) was isolated.

(ii) The bark (21 kg) was percolated at room temperature with light petroleum (60 l.) and then with ether (40 l.). The ethereal extract gave crude flindissol (172 g) but alkaloids were absent.

The light petroleum extract was concentrated and kept in the refrigerator for several weeks. The supernatant liquid was decanted from some dark amorphous material and the solvent removed from it. The residual oil was extracted repeatedly with warm 5% HCl (2·5 l.) and the crude alkaloids recovered from the acid extract. Repetition of the acid extraction gave a dark brown partly crystalline residue, which after extensive chromatography on alumina and recrystallization from methanol eventually yielded maculine (0·3 g).

The oil from which the alkaloid had been removed was diluted with ether, the solution washed thoroughly with water, and then extracted several times with 5% Na_2CO_3 and 5% NaOH.

The "acid" fraction yielded no crystalline substance, but the "phenolic" fraction on distillation gave a fraction, b.p. 140–200 °C/0·01 mm, which on refrigeration deposited a crystalline solid (0·12 g). Recrystallization from benzene gave colourless prisms, m.p. 156–157 °C, undepressed by admixture with collinol (Found: C, 62·3; H, 4·3%. Calc. for $C_{10}H_8O_4$: C, 62·5; H, 4·2%).

The "neutral" fraction was saponified with 10% aqueous alcoholic KOH for 10 days at room temperature. The unsaponifiable fraction, isolated as usual, was dissolved in the minimum of boiling ethanol and the solution refrigerated for 1 week. The crystalline material (7·6 g) was collected and recrystallized in turn from ether, acetone, and then repeatedly from ethanol yielding shining white flakes, m.p. 138–139 °C, undepressed by authentic β-sitosterol, $[\alpha]_D^{18°}$ −32 °C (*c*, 1% in chloroform) (Found: C, 84·3; H, 12·1%. Calc. for $C_{29}H_{50}O$: C, 84·0; H, 12·2%). The acetate had m.p. 131–132 °C (Found: C, 81·3; H, 11·5%. Calc. for $C_{31}H_{52}O_2$: C, 81·5; H, 11·5%).

(*e*) *Extraction of* F. dissosperma *Wood*.—The milled wood (2·2 kg) was extracted at room temperature in turn with light petroleum, ether, acetone, and methanol. No pure substance could be isolated from the light petroleum or methanol extracts, but by the usual procedures of acid extraction and chromatography, dictamnine was obtained from the ether extract (45 mg) and the acetone extract (33 mg).

III. Acknowledgments

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THE ISOLATION AND IDENTIFICATION OF 5-HYDROXYPIPERIDINE-2-CARBOXYLIC ACID FROM *LEUCAENA GLAUCA* BENTH.

By M. P. Hegarty*

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Summary

The isolation and identification of 5-hydroxypiperidine-2-carboxylic acid from the leaves of *L. glauca* Benth. by procedures using ion-exchange resins and chromatography are described. This imino acid has been synthesized and the resulting diastereoisomers separated by chromatographic techniques. The stereochemistry of the natural and the synthetic compounds is discussed.

I. Introduction

As part of an investigation of the nitrogenous constituents and nitrogen metabolism of some subtropical legumes, a study has been made of the free amino acids of *Leucaena glauca* Benth., using chromatographic techniques. *L. glauca* is a small tree which Engler and Prantl (1931) place in the subfamily Mimosoideae of the family Leguminoseae. Figure 1 shows a two-directional chromatogram of the free amino acids of the leaves of *L. glauca*. The unusual features of the chromatogram are: (i) the occurrence of mimosine (leucenol), β-(*N*-(3-hydroxy-4-pyridone)-α-aminopropionic acid); (ii) the presence of pipecolic acid in high concentration, and (iii) the presence of an unidentified ninhydrin positive compound designated as unknown *P*.

Unknown *P* gave with ninhydrin a blue-purple colour very similar to that of pipecolic acid, which fluoresced cherry-pink in ultraviolet light. With isatin, a deep blue-green colour was produced, and with vanillin a red colour formed overnight (Curzon and Giltrow 1954). These colour tests suggested that unknown *P* was one of the other isomeric piperidinecarboxylic acids, or a substituted derivative of these. Work has begun on the isolation of this compound when it was learned from Professor F. C. Steward (personal communication, 1955), Botany Department, Cornell University, that the properties of unknown *P* corresponded very closely with those of 5-hydroxypipecolic acid, a new imino acid which had been recently isolated in his Laboratory from the seeds of *Baikiaea plurijuga* (Grobbelaar, Pollard, and Steward 1955). Steward and co-workers had also shown that this compound occurs in the fruit of the edible date (*Phoenix dactylifera*) and a sample of this extract was kindly supplied by Professor Steward. It was soon shown that the compounds in *L. glauca* and in the date were chromatographically identical. About this time Virtanen and Kari (1955), who had earlier isolated 5-hydroxypipecolic acid from *Ceratonia siliqua* (Virtanen and Kari 1954) and from the palm *Rhapis flabelliformis* Ait., reported the isolation of both 5-hydroxypipecolic acid and an isomeric compound,

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which, it was claimed, was 4-hydroxypipecolic acid from *Acacia pentadena*. It was therefore considered desirable to establish the identity of unknown *P* in *L. glauca* by isolation and direct comparison with the other isolates, and with synthetic 5-hydroxypipecolic acid.

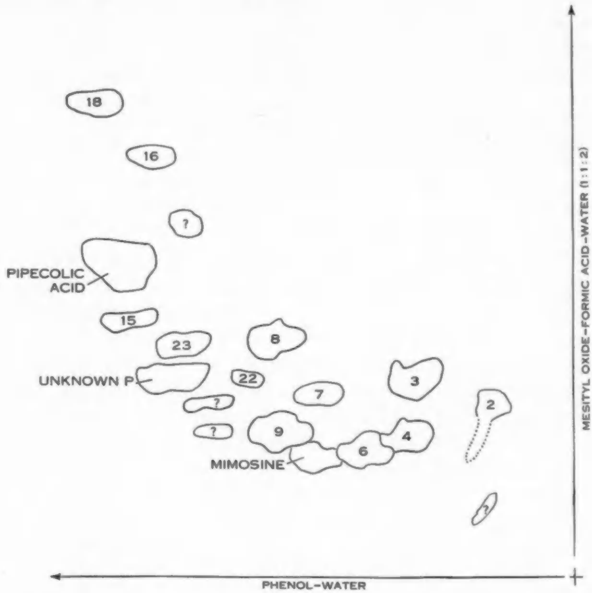

Fig. 1.—Chromatogram of the alcohol-soluble nitrogen compounds from the leaves of *L. glauca*.
2, aspartic acid ; 3, glutamic acid ; 4, serine ; 6, asparagine ; 7, threonine ; 8, α-alanine ; 9, glutamine ; 15, proline ; 16, valine ; 18, leucine(s) ; 22, β-alanine ; 23, γ-aminobutyric acid. Numbers follow the convention of Grobbelaar, Pollard, and Steward (1955).

II. Isolation and Characterization of Unknown *P*

The isolation of unknown *P* from an 80 per cent. ethanol extract of the leaves is described in detail in Section V. The amino acids were separated from the neutral and acidic substances using a cation-exchange resin " Zeokarb 215 " followed by displacement with ·1N hydrochloric acid. Since both pipecolic acid and γ-aminobutyric acid, which were major constituents of the extract, remained on the column after all the unknown *P* had been displaced, a partial purification was obtained. The substance was further purified using " Zeokarb 216 " and was finally obtained in crystalline form after chromatography on a cellulose column. The isolate was shown to be identical with respect to melting point, chromatographic position, and colour reactions with the isolate from *B. plurijuga*, and their identity was proven conclusively by means of the matched infra-red absorption spectra.

III. Synthesis of 5-Hydroxypipecolic Acid

The isolates from *B. plurijuga*, *C. siliqua*, and *R. flabelliformis* had been identified by chromatographic comparison with a synthetic sample of 5-hydroxypipecolic acid obtained from Dr. F. E. King (King, King, and Warwick 1950), which as mentioned by the Cornell workers had undergone some decomposition since its preparation. The oxidation experiments of Virtanen and Kari (1954) supported the placing of the hydroxyl group at position 5 and it was decided to confirm these results by an unequivocal synthesis and to study the configuration of the natural and synthetic material which had not previously been done. 5-Hydroxypicolinic acid was synthesized according to the method of Duesel and Scudi (1949) and the product was shown to be chromatographically homogeneous. Catalytic hydrogenation of this substance, whether in the form of its hydrochloride or as a suspension in distilled water, produced two distinct ninhydrin positive compounds (R_F phenol 0·92, 0·75) which could be partially separated by crystallization and were completely separated using a cellulose column. The compound of higher R_F value had the empirical formula $C_6H_{11}O_2N$ and was identified as DL-pipecolic acid by melting point, mixed melting point, and co-chromatography with an authentic sample.

The other ninhydrin positive substance had formula $C_6H_{11}O_3N$. On a butanol-acetic acid chromatogram the substance appeared to be chromatographically homogeneous and identical with naturally occurring 5-hydroxypipecolic acid. However, in collidine-lutidine (3 : 1) the compound was resolved into two well-defined spots (R_F 0·42, 0·38). The substance of higher R_F was isolated by paper chromatographic techniques and shown to be chromatographically identical with the natural material. The compound having the lower R_F was obtained in pure form by repeated recrystallization of the mixture from aqueous ethanol. During the hydrogenation of 5-hydroxypicolinic acid two asymmetric centres are formed resulting in the probable production of two racemates, which would be designated as DL-5-hydroxypipecolic acid and DL-*allo*-5-hydroxypipecolic acid.

After this synthesis had been completed, Cohen *et al.* (1956) reported the synthesis of 5-hydroxypipecolic acid starting from δ-hydroxylysine. These authors were able to separate the resulting 5-hydroxy-L-pipecolic acid and *allo*-5-hydroxypipecolic acid by ion-exchange chromatography and by paper chromatography in a basic solvent system. More recently, Witkop and Foltz (1957) have reported the isolation of the substance from dates and the determination of its configuration. These authors have shown conclusively that the configuration of the naturally occurring compound is exactly analogous to that of hydroxy-L-proline, having the substituents in the *trans*-position. Therefore, it would appear that the synthetic material which is chromatographically identical with the natural material is DL-5-hydroxypipecolic acid and that the compound of lower R_F value is DL-*allo*-5-hydroxypipecolic acid.

When the hydrogenation of 5-hydroxypicolinic acid is carried out in dilute ammonium hydroxide solution (pH 12) no pipecolic acid is formed—only the diastereoisomeric 5-hydroxypipecolic acids, and prolonged hydrogenation of these under either acid or alkaline conditions produces no pipecolic acid. There

appears to be no reference in the literature to any abnormal behaviour of 3-hydroxypyridine on catalytic hydrogenation in acid solution, and as yet the formation of large amounts of pipecolic acid during the hydrogenation of 5-hydroxypicolinic acid is not fully understood. It may involve elimination of water to form an unsaturated intermediate which is then reduced to pipecolic acid.

IV. Experimental

Melting points are uncorrected.*

(*a*) *Isolation of Unknown* P.—Freshly cut leaves of *L. glauca* (2 kg) were thoroughly extracted with cold 80% ethanol and the filtered extract concentrated under reduced pressure. The red oil was dissolved in water (1 l.) and absorbed on a column of "Zeokarb 215" (H^+ form) 4 by 48 cm at a flow rate of 0·5 ml/min. Carbohydrates and other non-ionic impurities, as well as organic and inorganic anions, were removed by washing with distilled water (4 l.). Small-scale experiments had shown that if the basic substances were displaced with 1N HCl, unknown *P* appeared in the eluate with aspartic and glutamic acids, serine, threonine, valine, β-alanine, and others while pipecolic acid and most of the γ-aminobutyric acid remained on the column. The eluate was collected in 30 ml fractions, 75 fractions being collected in all. Fractions 63 onward were found to contain mainly 5-hydroxypipecolic acid and these were bulked, taken to dryness, and the hydrochlorides of the amino acids converted to the free acids by absorption on "IR 120" (H^+ form) and elution with 2N NH_4OH. The ammonia eluate was concentrated to dryness, dissolved in water (10 ml), and adsorbed on a column of "Zeokarb 216" in the H^+ form. The column was eluted with water (pH 7) and the eluate collected in 10 ml fractions. Those fractions containing only unknown *P* were united and on concentration gave a clear glass which could not be induced to crystallize. Final purification was effected using a cellulose column and ethanol-acetic acid-water (90 : 2 : 8) which removed traces of valine and γ-aminobutyric acid and allowed the substance to crystallize. Crystallization from methanol-acetone and, finally, from aqueous acetone gave 5-hydroxypipecolic acid (63 mg) as fine white needles which have no true melting point but begin to darken at 250 °C and decompose without melting above 260 °C, $[\alpha]_D^{25}$ —10·1 (Found: C, 49·5; H, 7·5; N, 9·9%. Calc. for $C_6H_{11}O_3N$: C, 49·6; H, 7·6; N, [illegible]·7%).

Chromatographically the isolate was identical with that of Grobbelaar, Pollard, and Steward (1955) in four separate solvent systems and gave the same colour reactions. Finally, its infra-red spectrum was identical with that of the isolate from *B. plurijuga* as determined by the KBr disk technique.

(*b*) *Synthesis of the Two Diastereoisomeric* DL-*5-Hydroxypipecolic Acids*.—5-Hydroxypicolinic acid was synthesized according to the method of Duesel and Scudi (1949) and was obtained as the crystalline monohydrate, m.p. 270–272 °C (decomp.) (lit. 269–270 °C) (Found: C, 51·6; H, 3·9%. Calc. for $C_6H_5O_3N$: C, 51·8; H, 3·6%). Only one spot resulted when the compound was chromatographed in three separate solvents (Hulme 1955).

5-Hydroxypicolinic acid (1 g) was suspended in distilled water (50 ml) and HCl (1·0N; 7 ml) added. When the solid had dissolved, Adams's catalyst (50 mg) was added, and the solution hydrogenated at 2 atm pressure for 15 hr. The catalyst was filtered-off and the imino acid hydrochlorides converted to the free bases by absorption on "Dowex 50" (H^+ form) and elution with 2N NH_4OH. Removal of the ammonia left a white crystalline solid, an aliquot of which was chromatographed on Whatman No. 1 paper in water-saturated butanol-acetic acid (9 : 1) giving two ninhydrin positive spots (R_F 0·22 and 0·12). The crystalline solid was taken up in ethanol-acetic acid-water (90 : 2 : 8) (2 ml) and placed on a cellulose column (3 by 40 cm) which

* Melting points were determined between glass cover-slips on a Fisher melting point block. As many of the compounds in this investigation melted with decomposition at temperatures above 250 °C, the m.p. was first determined in the usual way, and a second sample was placed on the block at 10 °C below the observed m.p. and heated at the rate of 1 °C/min and the m.p. recorded.

had been equilibrated with the same solvent system. The chromatogram was developed with this solvent at a flow rate of 1 ml/hr and 10 ml fractions were collected (150 in all) and examined by one-directional chromatography. A clean separation of the two substances was obtained and the fractions containing only substance R_F 0·22 were combined, concentrated to dryness, and the white solid crystallized from anhydrous methanol, and, finally, from aqueous acetone as shining flakes (452 mg), m.p. 265–266 °C (decomp.) undepressed on admixture with an authentic sample of DL-pipecolic acid (Found: C, 55·6; H, 8·6%. Calc. for $C_6H_{11}O_2N$: C, 55·8; H, 8·5%). The crystalline material and authentic pipecolic acid were mixed and chromatographed in the three solvent systems mentioned above. In every case only a single spot was obtained.

The fractions containing only 5-hydroxypipecolic acid were combined and concentrated to dryness. Crystallization from aqueous methanol gave white needles, m.p. 232–235 °C. This material formed only one spot when chromatographed in butanol-acetic acid and gave the following analytical values (Found: C, 49·7; H, 7·8; N, 9·5%. Calc. for $C_6H_{11}O_3N$: C, 49·6; H, 7·6; N, 9·7%). However, when collidine-lutidine was used as the solvent, two separate spots (R_F 0·42, 0·38) were obtained. A dilute solution of the mixture was applied as a streak to 12 washed Whatman No. 3 papers and chromatographed in collidine-lutidine. The two ninhydrin positive areas were located on a test strip, cut out, and the material eluted with 30% aqueous ethanol giving small amounts of the two diastereoisomers in crystalline form. The racemate of higher R_F value was identical with the natural material, in three solvents and on the basis of Witkop's identification of the natural material as 5-hydroxy-L-pipecolic acid is DL-5-hydroxypipecolic acid. The other diastereoisomer, DL-*allo*-5-hydroxypipecolic acid, was also obtained by repeated crystallizations of the mixture from aqueous ethanol and had m.p. 236–237 °C. The infra-red spectra of the two diastereoisomers were measured, but that of the normal form was not identical with that of the natural 5-hydroxypipecolic acid, presumably because the synthetic material is a racemate. Differences have been observed between the infra-red spectra of the optically active and racemic forms of proline, pipecolic acid, and azetidine-2-carboxylic acid (Fowden 1956).

When the hydrogenation was carried out in dilute ammonium hydroxide solution (pH 12) no pipecolic acid was formed. Paper chromatographic comparison of the relative amounts of the racemates formed under acidic and alkaline conditions showed that in the former case the *allo*-isomer predominated, but in the latter the racemates were present in almost equal amounts.

V. Acknowledgments

The author is grateful to Professor F. C. Steward for making some of his results available in advance of their publication, for samples of naturally occurring 5-hydroxypipecolic acid, and in the final stages of the investigation for the hospitality of his laboratory and for helpful discussions.

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SHORT COMMUNICATIONS

NEW COMPOUNDS OF MOLYBDENUM(III) WITH BIDENTATE LIGANDS*

By M. C. Steele†

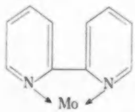
The coordination of bidentate ligands such as *o*-phenanthroline and 2,2′-dipyridyl with molybdenum(III) has not been reported previously.

Octahedral chelate complexes of the type $Mo(phen)_3X_3$ and $Mo(dipy)_3X_3$ (X=Cl, Br, I) have been prepared. Magnetic susceptibilities consistent with the existence of three unpaired electrons are interpreted as arising from $4d^25s5p^3$ binding.

Attempts to form perchlorates by replacement of bromine in the bromo complexes failed.

The described bidentates appear to be very stable, thus indicating that the lower *d* orbitals are used in the binding.

Because there is no electron pairing as evidenced by the effective μ value of 3·8, it is probable that only single bond structures exist such as:



Experimental

The halogen bidentates were prepared from hexahalides, R_3MoX_6, with effective magnetic moments of 3·8 Bohr magnetons (B.M.).

(i) *Tris-o-phenanthroline Molybdenum(III) Chloride.*—$(NH_4)_3MoCl_6$ (0·5 g) was dissolved in water and ethanol and a few ml of HCl added. To this solution was added *o*-phenanthroline alcoholic solution (0·5 g). The resulting red solution was concentrated under reduced pressure at 60 °C. The dark red product was washed with water, then with ethanol, and dried (Found: Mo, 12·2; Cl, 13·5%. Calc. for $Mo(phen)_3Cl_3$: Mo, 12·4; Cl, 13·6%).

Tris-*o*-phenanthroline molybdenum(III) chloride is a dark red powder, slightly soluble in ethanol and acetone, but insoluble in water or nitrobenzene. Mol. cond. in absolute ethanol at 25 °C for M/8000=42·6 r.o., $\mu_{eff.}$=3·83 B.M.

Each of the other preparations was carried out in a similar manner. The bromide preparations starting with K_3MoBr_6 gave at once orange coloured precipitates.

(ii) *Tris-o-phenanthroline Molybdenum(III) Iodide.*—This compound is a chocolate coloured powder, slightly soluble in ethanol and acetone but insoluble in water or nitrobenzene (Found: Mo, 9·0; I, 36·5%. Calc. for $Mo(phen)_3I_3$: Mo, 9·1; I, 36·1%). Mol. cond. in absolute ethanol at 25 °C for M/8000=43·2 r.o., $\mu_{eff.}$=3·84 B.M.

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(iii) *Tris-o-phenanthroline Molybdenum(III) Bromide.*—This compound is an orange coloured powder, insoluble in water and ethanol but soluble in nitrobenzene (Found : Mo, 10·5 ; Br, 26·3%. Calc. for $Mo(phen)_3Br_3$: Mo, 10·5 ; Br, 26·3%). Mol. cond. in nitrobenzene at 25 °C for M/1000=43·6 r.o., $\mu_{eff.}$=3·84 B.M.

(iv) *Tris-2,2'-dipyridyl Molybdenum(III) Chloride.*—This compound is a dark red powder, slightly soluble in ethanol and acetone, insoluble in water and nitrobenzene (Found : Mo, 14·4 ; Cl, 15·8%. Calc. for $Mo(dipy)_3Cl_3$: Mo, 14·3 ; Cl, 15·9%). Mol. cond. in absolute ethanol at 25 °C for M/8000=42·6 r.o., $\mu_{eff.}$=3·66 B.M.

(v) *Tris-2,2'-dipyridyl Molybdenum(III) Iodide.*—This compound is a chocolate coloured powder, slightly soluble in ethanol and acetone, insoluble in water and nitrobenzene (Found : Mo, 10·0 ; I, 40·1%. Calc. for $Mo(dipy)_3I_3$: Mo, 10·2 ; I, 40·2%). Mol. cond. in absolute ethanol for M/8000=44·1 r.o., $\mu_{eff.}$=3·84 B.M.

(vi) *Tris-2,2'-dipyridyl Molybdenum(III) Bromide.*—This compound is an orange-yellow powder, insoluble in water and ethanol but soluble in nitrobenzene (Found : Mo, 11·8 ; Br, 29·3%. Calc. for $Mo(dipy)_3Br_3$: Mo, 11·8 ; Br, 29·2%). Mol. cond. in nitrobenzene at 25 °C for M/1000=45·3 r.o., $\mu_{eff.}$=3·84 B.M.

THE COMPLEX CHLORIDES OF MOLYBDENUM(III)*

By R. J. Irving† and M. C. Steele†

Three types of complex chlorides of molybdenum(III) have been reported namely, $R_2MoCl_5H_2O$, R_3MoCl_6, and $R_4MoCl_7.2H_2O$.

Of these the hexachloride has received by far the most attention and the values of 3·7–3·86 Bohr magnetons (B.M.) (Bose 1928 ; Tjabbes 1933 ; Klemm and Steinberg 1936) reported for the magnetic moment confirm the octahedral configuration of the molybdenum bonds resulting from d^2sp^3 hybridization.

For the sake of completeness the hitherto unknown lithium salt has been prepared. It is much more hygroscopic than the other alkali metal salts and, unlike them, cannot be prepared in the anhydrous state.

The other two series of chlorides apparently involve coordination numbers of 5 and 7 respectively, although the pentachloride has been formulated as an octahedral complex, for example, $K_2[MoCl_5H_2O]$ (von Foerster and Fricke 1923).

Molybdenum(VI) has a marked tendency to form bonds to oxygen. This tendency seems to persist in all oxidation states and in oxidation state (III), compounds such as $MoOCl.4H_2O$ (Wardlaw and Wormell 1924, 1927) are known. This latter compound has been isolated in two forms, presumably *cis-* and *trans-*isomers. This isomerism could only arise if the water molecules were coordinated to molybdenum to give an octahedral structure.

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Pentachlorides

Unfortunately, magnetic data cannot distinguish between the two structures $M_2[MoCl_5]H_2O$ and $M_2[MoCl_5H_2O]$ as either can be formulated with three unpaired electrons. The magnetic moment of $(NH_4)_2MoCl_5H_2O$ has been determined as 3·78 B.M., corresponding to the theoretical value for three unpaired electrons. Of the known types of hybridization which can produce coordination number 5 (Kimball 1940), dsp^3, d^2sp^2, and d^2p^3 satisfy the magnetic data without the necessity of promoting electrons to higher levels.

Potassium hexachloromolybdate(III) is an "inner orbital" complex (Taube 1952) having three singly occupied $4d$ orbitals and as the ammonium pentachloroaquomolybdate(III) is similar in its reactivity, it also probably has the three

TABLE 1

MAGNETIC MOMENTS OF MOLYBDENUM CHLORIDE

Compound	$\chi_M \times 10^{-6}$	Diamagnetic Correction	$\chi_M \times 10^{-6}$ (corr. for diamagnetism)	Magnetic Moment (μ)
$(NH_4)_3MoCl_6$	5986	160	6146	3·83
K_3MoCl_6	5604	165	5769	3·70
$Li_3MoCl_6.9H_2O$	5796	310	6106	3·82
$(NH_4)_2MoCl_5.H_2O$	5853	140	5993	3·78
$(NH_4)_3MoCl_6.NH_4Cl.H_2O$ ..	5563	207	5770	3·70
$K_3MoCl_6.4KCl.6H_2O$	3980	395	4375	3·2

singly occupied orbitals. Either d^2sp^2 or d^2p^3 hybridization satisfies this requirement and each of the hybrid types presupposes a tetragonal pyramidal structure. The other hybrid type, dsp^3, would leave unoccupied one $4d$ orbital and this should confer much greater reactivity on the molecule.

The dimeric structure $[Cl_4MoCl_2MoCl_4]^{4'}$ with two halogens bridging the molybdenum atoms has hitherto not been considered. This also should have a magnetic moment of about 3·8 B.M., but as the two molecules of water are outside the coordination entity they should be lost at 100 °C. The possibility that the water molecule is not merely present as water of crystallization but is part of the coordination body must receive serious consideration as this water molecule can only be removed by heating to 150 °C and then only by decomposition of the compound. On this basis and by comparison with its chromium analogue the octahedral monomeric structure $[MoCl_5H_2O]^{2'}$ is preferred.

Heptahalides

This series, first reported by Carobbi (1928), is represented only by the compound $(NH_4)_4MoCl_7.2H_2O$. Again the coordination number of the central atom is uncertain. The compounds have magnetic moments (see Table 1) corresponding to three unpaired electrons which eliminates coordination number 7, unless promotion of electrons to the $5d$ level is to be invoked. Similarly, coordination number 8, which is well established for molybdenum in the stable

compound $K_4Mo(CN)_8$, can be discarded in this case, as it does not satisfy the magnetic criterion.

A more reasonable assumption supported by the magnetic data is that the compound is a double salt $(NH_4)_3MoCl_6.NH_4Cl.2H_2O$.

For the compound $(NH_4)_4[MoCl_7.H_2O]$ by comparison with $K_4Mo(CN)_8$ we would expect a conductivity of about 510 mhos in aqueous solution (M/1000). The observed value of 730 mhos is concordant with the six ions of the double salt in solution.

A study of the visible ultraviolet spectrum of solutions of $(NH_4)_3MoCl_6$ and $(NH_4)_4MoCl_7.2H_2O$ showed absorption peaks in each case at 215, 260, and 295 Å. Further, the percentage absorption in each case was the same when the solutions were of the same molybdenum concentration.

Apparently, this tendency to form double salts is common, as a well-defined substance $K_3MoCl_6.4KCl.6H_2O$ was also isolated. Its spectrum was identical with that of K_3MoCl_6 at the same molybdenum concentration.

Experimental

(*a*) *Lithium Hexachloromolybdate(III)*.—A mixture of molybdenum trioxide (20 g) and lithium carbonate (10 g) was dissolved in 4N HCl (200 ml). This solution was electrolysed in an atmosphere of CO_2 until the colour of the reduced solution was amber. A mercury cathode and a carbon anode were used and the anolyte was separated from the catholyte by a sintered-glass diaphragm. At the applied potential of 12 V the current was 3–4 A. After reduction, the solution was saturated with CO_2 and HCl (gas) and then evaporated under reduced pressure to a syrup which, unless seeded, was difficult to crystallize. The red crystals are hygroscopic (Found: Mo, 19·2; Cl, 42·6%. Calc. for $Li_3MoCl_6.9H_2O$: Mo, 19·5; Cl, 43·2%). The magnetic moment determined by the Gouy method was 3·82 B.M.

(*b*) *Ammonium Hexachloromolybdate(III)*.—This compound was prepared in a similar way to the lithium salt by electrolysis of ammonium molybdate (10 g) and ammonium carbonate (10 g) in 8N HCl (200 ml) (Found: Mo, 26·5; Cl, 58·6; N, 12·1%. Calc. for $(NH_4)_3MoCl_6$: Mo, 26·5; Cl, 58·6; N, 12·2%). The conductivity of an aqueous solution (M/1000) was 374 mhos. There was no significant hydrolysis within 15 min.

(*c*) *Potassium Hexachloromolybdate(III)*.—This compound was prepared by a modification of the method of Bucknall, Carter, and Wardlaw (1927). A solution prepared by dissolving molybdenum trioxide (20 g) in the minimum vol. of saturated KOH was acidified with 8N HCl (300 ml). This solution was electrolysed as described in the preparation of lithium hexachloromolybdate(III). The red reduced solution was saturated with HCl (gas) and cooled in the refrigerator. The red crystals which separated were washed with ethanol (Found: Mo, 22·5; Cl, 50·0%. Calc. for K_3MoCl_6: Mo, 22·3; Cl, 50·0%).

(*d*) *Ammonium Pentachloroaquomolybdate(III)*.—To molybdenum trichloride solution (100 ml; containing 33 g $MoCl_3$) was added NH_4Cl (10 mg) in water (90 ml). This resulting solution was concentrated at 70 °C under reduced pressure until crystallization began. On rapid cooling, followed by filtration, a brick-red product was obtained which was washed with 95% ethanol and finally with absolute ethanol (Found: Mo, 29·4; Cl, 54·3%. Calc. for $(NH_4)_2MoCl_5.H_2O$: Mo, 29·4; Cl, 54·3%). The effective magnetic moment of the compound dried *in vacuo* was 3·86 B.M. The conductivity of an aqueous solution (M/1000) was 265 mhos. Slight hydrolysis indicated by an increase in conductivity to 302 mhos was apparent after 15 min.

(*e*) *Heptachloro-Salt*.—Electrolytic reduction of molybdenum trioxide (10 g) and ammonium carbonate (10 g) in 8N HCl (200 ml) was carried out as in the preparation of lithium hexachloromolybdate(III). When reduction was complete as shown by the red colour of the catholyte and free evolution of hydrogen, ammonium carbonate (5 g) was added. Saturation with HCl (gas)

gave red crystals of the double salt which were washed with ethanol and dried in air (Found: Mo, 21·3; Cl, 55·0%. Calc. for $(NH_4)_3MoCl_6.NH_4Cl.H_2O$: Mo, 21·2; Cl, 54·9%). An aqueous solution of the salt at M/1000 dilution gave a conductivity of 730 mhos. No significant hydrolysis was apparent on standing for 15 min. The salt is paramagnetic with a moment of 3·7 B.M.

(*f*) *Decachloro-Salt.*—Impure potassium hexachloromolybdate(III), prepared according to the method of Bucknall, Carter, and Wardlaw (1927), was dissolved in a minimum volume of water and reprecipitated with ethanol. This brown salt was filtered and washed with ethanol (Found: Mo, 11·5; K, 32·6; Cl, 42·5%. Calc. for $K_3MoCl_6.4KCl.6H_2O$: Mo, 11·5; K, 32·7; Cl, 42·6%). The magnetic moment was 3·2 B.M. and the conductivity of an aqueous solution (M/1000) was 920 mhos.

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CHARGE DISTRIBUTION AND DIPOLE MOMENT OF PYRIDINE*

By R. D. Brown† and M. L. Heffernan†

The π-electron distribution in pyridine has been calculated recently using the SCFMO method (Brown and Heffernan 1957*a*). The charge distribution may also be calculated by a configuration interaction treatment as has been done for the simple two-centre systems $CH_2{=}NH_2^+$, $CH_2{=}NH$, $CH_2{=}N^-$ (Brown and Penfold 1956, 1957) and $CH_2{=}O$ (Brown and Heffernan 1957*b*). We have used the Parr-Pariser (1953) treatment, including limited configuration interaction. The ground state charge distribution is obtained by mixing together the charge distributions of all the singlet configurations that have the ground state symmetry, namely $^1A_1$. In the present calculations we have included only those configurations which arise from the excitation of an electron from the two highest bonding orbitals in pyridine up to the lowest two antibonding π-orbitals (in the case of benzene these correspond to doubly degenerate bonding and antibonding orbitals respectively). We thus obtain two singlet configurations

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Φ_1 and Φ_2, which mix with the ground state configuration Φ_0, to give the final ground state wave-function :

$$\Psi_0 = A_0\Phi_0 + A_1\Phi_1 + A_2\Phi_2.$$

The coefficients A_0, A_1, and A_2 were obtained by solution of the appropriate secular equations using the values of the matrix elements derived in a treatment of the ultraviolet spectrum of pyridine (Brown, Heffernan, and Penfold, unpublished data). The charge distribution in the ground state was obtained from these coefficients using formulae analogous to that given by Taylor (1951), but simplified by the assumption of zero differential overlap (Pariser and Parr 1953). The π-electron densities $P_{\mu\mu}$ obtained in this way are compared with those previously found by the SCF method in Table 1.

As in the case of previous calculations (Brown and Heffernan 1957*a*, 1957*b* ; Brown and Penfold 1956, 1957) the configuration-interaction (ASMOCI) charge densities correspond to an overall smaller charge separation than do the SCF values. The disparity between the two sets of results is about the same as in former calculations, indicating that the configurations of $^1A_1$ symmetry with higher energies than those included in the present calculations probably do not influence the charge distribution appreciably.

TABLE 1

CHARGE DISTRIBUTION IN PYRIDINE

Method	P_{NN}	$P_{\alpha\alpha}$	$P_{\beta\beta}$	$P_{\gamma\gamma}$
SCFMO ..	1·061	0·999	0·983	0·974
ASMOCI ..	1·027	1·013	0·987	0·973
SCE*	1·031	1·000	0·991	0·987

* These values were obtained from the SCFMO values by halving the formal charges found by the SCF method.

The third charge distribution listed in Table 1 is an estimate of the result which would be obtained by the self-consistent electronegativity (SCE) method (Brown and Heffernan 1957*a*). The full SCE calculations have not so far been performed for pyridine but the present values have been estimated using the observation that charge separations found by the SCE method are very close to half those found by the SCFMO method.

The present results may be used to evaluate the π-electron contribution to the molecular dipole moment. In the case of formaldehyde (Brown and Heffernan 1957*b*) the dipole moment could be accounted for entirely in terms of hybridization moments plus a small π-electron moment, the latter being derived from SCE charge distribution. The same analysis may now be applied to the pyridine system. We have used the SCE charge distribution and the geometry previously quoted (Brown and Heffernan 1957*a*). The valence electrons are symmetrically disposed around each carbon atom so that no contribution is made to the molecular dipole. The moments arising from

hybridized valence orbitals for the hydrogen atoms cancel one another in the case of the β- and α-hydrogens, but the valence orbital of the γ-hydrogen atom results in a hybridization moment with the negative end directed towards the nitrogen atom. This reinforces the hybridization moment arising from the nitrogen valence electrons owing to the uncompensated electron in the sp^2 lone-pair orbital. When the small π-electron moment is added to these hybridization moments the total comes to 2·33 D (Table 2), which is in surprising agreement with the experimental value of 2·25 D (Wesson 1948). This strongly suggests that there is no appreciable polarization of the C—N σ-bonds, that is, that these bonds are purely covalent.

TABLE 2

THE DIPOLE MOMENT OF PYRIDINE

Contribution	Value (D)
π-electron moment..	0·356
H-hybridization	0·199
N-hybridization	1·778
Total	2·333

The fact that the σ-electron polarization is negligible may alternatively be deduced from the very small polarization of π-electrons found in the present calculations. Since σ-electrons are less easily polarized than π-electrons, the σ-electron polarization must be expected to be even smaller and so for most purposes negligible. A similar conclusion has been reached for the C—O σ-electrons in formaldehyde, and the same probably applies therefore to conjugated heterocyclic systems generally.

One of us (M.L.H.) gratefully acknowledges the award of a C.S.I.R.O. studentship.

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THE USE OF POTASSIUM CHLORIDE DISKS IN THE INFRA-RED EXAMINATION OF FIBROUS CELLULOSE AND OTHER SOLID MATERIALS*

By H. G. Higgins†

Potassium bromide was used in the early work on the pressed alkali halide disk method for the infra-red examination of solid samples by Schiedt and Reinwein (1952), Stimson and O'Donnell (1952), Anderson and Woodall (1953), and Hausdorff (1953). For this reason, probably, potassium bromide continues to be used in preference to potassium chloride, which has several advantages, as pointed out by Hales and Kynaston (1954). Potassium chloride has a lower chemical reactivity and a greater stability to heat than potassium bromide, and the slightly higher pressure required for flow is immaterial in practice. It is less hygroscopic and easier to grind to a satisfactory particle size without taking up moisture. Ford and Wilkinson (1954) recognized that potassium chloride was as suitable as potassium bromide, and that sodium chloride, while otherwise satisfactory, required a much higher pressure owing to its greater lattice energy.

Having examined the relative merits of these three halides, we would support the use of potassium chloride. Stable disks and well-defined spectra of a range of solid materials, mostly of high molecular weight, have been obtained without the use of a dry box. With potassium chloride disks, the absorption over most of the rock-salt region of the spectrum does not exceed 2 or 3 per cent., and with appropriate care only very small absorption bands at 2·9 and 6·1 μ remain, owing to the water present. With potassium bromide, changes have been observed in spectra with time (Barker *et al.* 1956) and difficulties have been encountered in the study of simple mixtures (Bak and Christensen 1956); it is not known whether these disadvantages apply also to potassium chloride disks. Farmer (1955) has suggested that misleading results may sometimes be obtained by the disk technique when it is applied to compounds containing hydroxyl groups. However, it would be unfortunate if the considerable advantages of the alkali halide disk method over the use of mulls were to be underestimated on account of relatively minor difficulties. The absorption bands of the paraffin tend to mask those of the specimen, mulling does not lend itself readily to quantitative treatment or to keeping the dispersed sample for further examination, the Christensen effect is likely to be more pronounced with mull spectra (Ford and Wilkinson 1954) and very small samples cannot be dealt with as readily as by the disk technique.

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The procedure now in use in this Laboratory has been adapted from the suggestions of various previous workers. It has been found satisfactory for cellulose and various derivatives of a fibrous nature, as well as for crystalline materials.

Method

The disk contains usually 0·5 per cent. sample and 99·5 per cent. KCl. The sample concentration may be lowered if bands of high intensity are being studied. The KCl is prepared as described by Hales and Kynaston (1954) by precipitation from solution with ice-cold concentrated HCl. Reference has been made by previous workers to the undesirable influence of even slight amounts of impurities in A.R. grade reagents on the behaviour of the halide in the disk technique. Precipitation of KBr and NaCl by the same method as used for the KCl, but using the appropriate reagents, was found in the present work to improve greatly the quality of the disks and the spectra observed. The HCl bands can be removed entirely from the KCl spectrum by overnight baking of the precipitate at 450 °C. The fibre sample is ground as fine as possible (—60 mesh/in) in a Wiley laboratory mill and 0·75 mg is weighed out on a microbalance (an accuracy of *c.* 0·01 mg is required). The KCl is added to make a total weight of 0·15 g. Both the final grinding and mixing of the sample are carried out manually in an evaporating dish with a somewhat roughened bottom, using a glass pestle with a ground surface. This method has been found more satisfactory for fibrous materials than the use of various mechanical homogenizers (including a dental "amalgamator" for which a steel capsule was made). A vacuum mould and screw press were supplied by Messrs. Hilger and Watts Pty. Ltd. and are similar to the design of Ford and Wilkinson (1954, Figs. 1 and 2). With the lower die already in place, the whole mould assembly, including the loose upper die, is preheated on a hot plate to *c.* 60 °C. The powder is transferred quantitatively to the mould through a short-stemmed funnel, and after inserting the upper die and plunger, the assembly is evacuated. The air pressure is reduced to about 0·5 mm Hg, and after 3–5 min, pressure is applied to the plunger by means of the screw press. An expansion piece is inserted between the plunger of the vacuum mould and the screw. This is heated with a Bunsen burner, mounted rigidly behind it to provide higher pressure. Electrical heating could probably be used with greater convenience. (In some experiments carried out with a hydraulic press and gauge, a pressure of *c.* 8 tons on a disk 1 cm in diameter was found to give satisfactory results. The minimum sintering pressure for the various halides was measured by Ford and Wilkinson and found to be *c.* 40 ton/in^2 for KCl.) After about 5 min the expansion piece, which is hollow with inlet and outlet leads, is cooled by passing water through it, and the screw is loosened. To avoid cracking the disk, the die assembly is removed from the mould, inverted, and a V-shaped wire support is placed over the lower die, followed by a small ¼ in. thick, foamed "Nylon" cushion. The mould is then reassembled and the disk is extruded between the two dies by applying gentle pressure to the plunger, the V-support resting between the annular ledge of the cup and the outer part of the mould. This procedure obviates the necessity for a conical die and cylinder (Ford and Wilkinson 1954). For quantitative work the disk may be weighed after brushing away the squeeze-out, which may exceed 10% of the total powder. If the disk cannot be examined immediately it is kept under dry conditions: small screw-top jars with thin perforated metal foil trays resting on silica gel are convenient storage desiccators. After the first infra-red examination, each disk is labelled by attaching a ¼ in. wide paper strip to the edge with adhesive tape; this also facilitates subsequent handling. A cell has been devised which accommodates disk and label. In subsequent examination care is taken, of course, that the beam does not pass through the part of the disk covered by the adhesive strip. Spectra are recorded on a Grubb Parsons double-beam S4 spectrometer. The data given below were obtained with a NaCl prism, Nernst current 0·9 A, amplifier gain 6·0, slit setting 0·03, slit schedule 0·50 mm, and 30 min scan.

The original cellulosic materials were an α-cellulose pulp, prepared from *Eucalyptus* wood by Australian Paper Manufacturers Pty. Ltd., and an imported long-fibred bleached kraft pulp containing 7% pentosans. Acetylation of the α-cellulose was essentially according to the method of Hess and Ljubitsch (1928); details of the preparation of acetates, propionates, and butyrates

from the long-fibred pulp are given elsewhere (Higgins, McKenzie, and Harrington, unpublished data). The acetyl, propionyl, and butyryl determinations were made by Dr. K. W. Zimmermann and the staff of the C.S.I.R.O. Microanalytical Laboratory; *p*-toluenesulphonic acid was used in the hydrolysis.

Quantitative Aspects

The possibilities of using the disk technique quantitatively were indicated by Schiedt and Reinwein (1952) who substitute m/Fd for the molar concentration in the Beer-Lambert law to get

$$I = I_0 e^{-\varepsilon' m/F}, \qquad (1)$$

where m is the number of millimoles of sample in the disk, F is the surface area of the disk, d is its thickness, I and I_0 are the intensities of the emergent and incident radiation respectively, and ε' is the molar extinction coefficient of the material of the sample. Jensen (1954) has used potassium bromide disks in the infra-red determination of benzylpenicillin, and Kirkland (1955) has determined the reproducibility of various methods of sample preparation. From our experience we would not regard the disk technique as strictly quantitative, but the results obtained on a series of cellulose esters of varying degree of substitution will illustrate the degree to which quantitative measurements can be achieved without special measures beyond those mentioned above. For acetates the intensities of the $C=O$ stretching, $C-CH_3$ deformation (symmetrical), and $C-O-$ stretching bands* were measured and for propionates and butyrates only the $C=O$ stretching, the other bands being in inappropriate positions for quantitative work. Optical density at the frequencies of maximum absorption was measured in preference to integral absorption in order to test the applicability of Beer's law in respect to the degree of substitution of the cellulose. The concentration of cellulose ester dispersed in the potassium chloride was constant (0·5 per cent.) and in a typical series of 10 disks, the disk weight was 85 per cent. of the original powder weight, with a standard deviation of 2·9 per cent.

If m is now taken as referring to the number of millimoles of the substituent group in the disk, it follows that

$$m = \frac{10 W_s W_D x}{W_0 M}, \qquad (2)$$

where W_s, W_D, and W_0 are respectively the weights (in grams) of the sample in the disk, of the disk itself, and of the original powder (alkali halide plus sample), x is the percentage acyl content of the sample, and M is the molecular weight of the substituent group. Equation (1) can now be written:

$$I_1 = I_0 e^{-(D_0 + \varepsilon' m/F)}, \qquad (3)$$

where I_1 is the emergent intensity at a given value of x, and D_0 is the optical density arising from causes other than the substituent. If I_2 is the emergent intensity when $x=0$ (and therefore $m=0$) we get

$$I_2 = I_0 e^{-D_0}, \qquad (4)$$

* The assignments will not be discussed here; for general reference see Bellamy (1954).

so that

$$I_2/I_1 = e^{\varepsilon' m/F} \text{ or } \ln (I_2/I_1) = \varepsilon' m/F. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Thus, from (2) the molecular extinction coefficient ε is given by

$$\varepsilon = \frac{\varepsilon'}{\log_e 10} = \frac{W_0 MF}{10 W_s W_D} \cdot \frac{\log_{10} (I_2/I_1)}{x}. \quad \ldots\ldots\ldots\ldots \quad (6)$$

The value of I_2/I_1 is obtained as shown in Figure 1 from the ratio of the transmission percentages (100 − percentage absorption) at the bottom and top respectively of the vertical dotted lines through the absorption peaks. The method is similar to that used by Wright (1941); it is somewhat arbitrary, particularly where the band being measured is adjacent to other bands (as for the C—O— stretching vibration shown in Fig. 1).

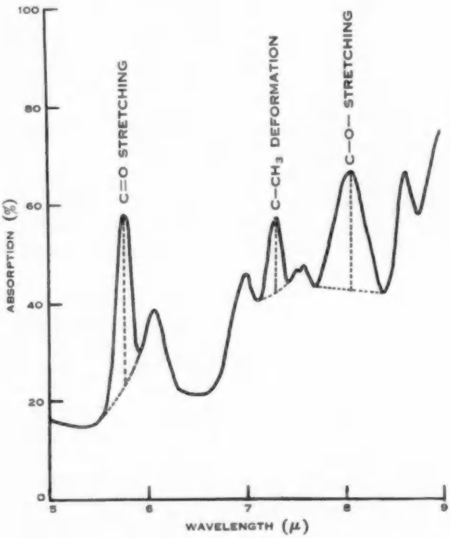

Fig. 1.—Method of estimating I_2/I_1 (see text).

In (*a*), (*b*), and (*c*) of Figure 2, the observed relationships between acetyl content and optical density are shown for a series of acetylated α-celluloses. That the scatter of the results around the Beer's law curve arises mainly from errors in the amount of cellulose acetate in the beam of the spectrometer rather than spectroscopic causes is shown by (*d*) in Figure 2, in which a smoother relationship between the optical densities connected with the C=O stretching and the C—O— stretching modes is apparent.

In Figure 3 data are shown relating to acetates, propionates, and butyrates prepared from a long-fibred bleached kraft pulp. The spectrum of this material, unesterified, is very similar to that of the eucalypt α-cellulose, despite the higher

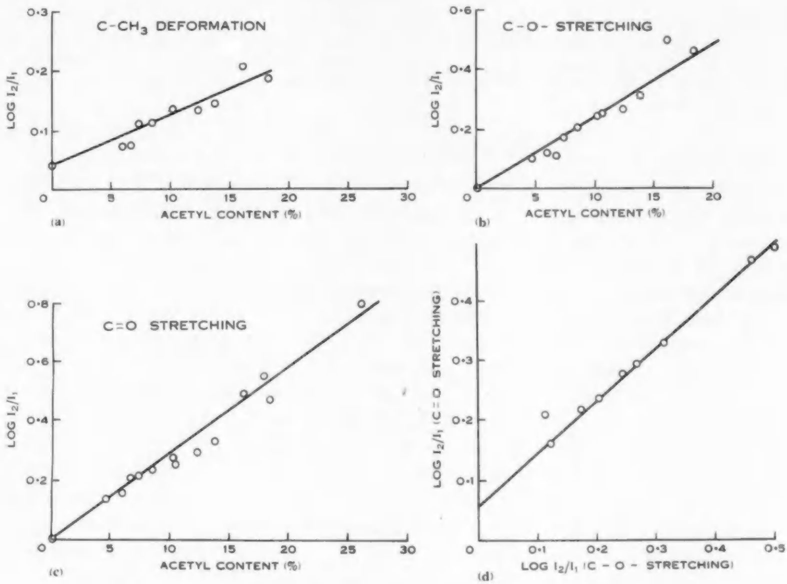

Fig. 2.—Intensity data for acetylated eucalypt α-cellulose.

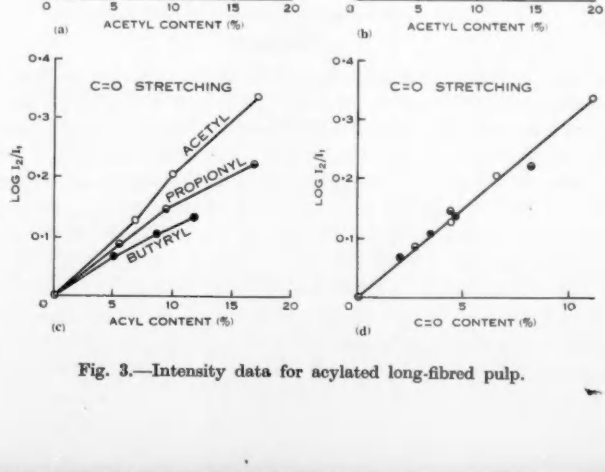

Fig. 3.—Intensity data for acylated long-fibred pulp.

hemicellulose content. Over the more limited range of acyl content studied the optical densities appear to be considerably lower than for the α-cellulose derivatives. These anomalies may arise mainly from differences in the capacity of the different materials to be dispersed adequately in the potassium chloride. The intensity of the C=O stretching band is independent of the size of the substituent group as shown in Figure 3 (*d*). Reasonable concordance with Beer's law is also shown here.

It can be seen from equation (**6**) that the slopes of the log (I_2/I_1) *v.* x plots are a measure of the molecular extinction coefficients. Taking $W_s=0{\cdot}00075$ g, $W_D/W_0=0{\cdot}85$, $M=43$ (CH_3CO-), and $F=\pi/4$ cm^2, we arrive at the following apparent values of ε for the absorption bands in the acetylated α-cellulose fibres :

C=O stretching	152
C–O– stretching	126
$C-CH_3$ deformation	68

These apply only under the conditions of this experiment, since the width of the absorption bands are of the same order as the spectral slit width (see e.g. Barnes *et al.* 1944) and because the extent to which the method of disk preparation affects the results is not known with certainty.

The skilled assistance of Mr. K. J. Harrington in the preparation of pellets, and of Mr. A. W. McKenzie and Mr. Harrington in the preparation of cellulose esters is gratefully acknowledged.

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STUDIES IN THE CHEMISTRY OF PHENOTHIAZINE*

III. ATTEMPTS TO PREPARE SOME PENTACYCLIC COMPOUNDS

By K. J. FARRINGTON† and W. K. WARBURTON†

In a search for compounds related to phenothiazine which might have greater anthelmintic activity than the parent compound, or which might give information about its mode of action *in vivo*, we have attempted the synthesis of 5,7-dithia-12,14-diazapentacene (I) and 5,12-dithia-7,14-diazapentacene (II). Preliminary results were discouraging because of the small yields of several of the intermediates, and because the two related compounds which were tested, the 6,13-quinol and the quinone derived from II (Fries, Pense, and Peters 1928) were found to be inactive against oxyurids in mice. This work has been discontinued, and we now report some experiments directed towards building up a second thiazine ring.

In Part II of this series (Farrington and Warburton 1956) it was shown that 1,3-dichloro-4,6-dinitrobenzene condensed readily with the sodium salt of 2-amino-4-chlorobenzenethiol to give 4,6-di-(2-amino-4-chlorobenzenethio)-1,3-dinitrobenzene (III). This compound suggested a route to compounds of class I, for a double Smiles rearrangement of the diacetyl derivative of III would give the 2,10-dichloro-derivative of I. Acetylation, rearrangement, and ring closure of III to give 2-(2-acetamido-4-chlorobenzenethio)-3-nitro-8-chlorophenothiazine (IV) was readily carried out, but a second rearrangement could not be induced by the action of alkali or sodium alkoxides in various ethanolic solvents, even in sealed vessels at temperatures of up to 150 °C.

The diacetyl derivative of III was difficult to purify and benzoylation was more satisfactory, but, similarly, the dibenzoyl derivative could not be made to undergo a second rearrangement, although the first rearrangement and ring closure proceeded well. The failure of IV to undergo Smiles rearrangement recalls that of 2-acetamido-4,3′-dichloro-2′-nitrodiphenyl sulphide (Farrington and Warburton 1956), and may be due to the same cause. On the other hand, it may be due to the presence of a nitro-group *para* to the imino-group, and, therefore, oxidizable readily to a quinone imine type of compound.

Attempts to prepare I itself from both the diacetyl and dibenzoyl derivative of 4,6-di-(2-aminobenzenethio)-1,3-dinitrobenzene gave similar results, and the second acetyl or benzoyl group resisted alcoholysis. For that reason, and because of the position of the ultraviolet absorption maxima, we have assigned the acetyl or benzoyl group to the exocyclic nitrogen atom.

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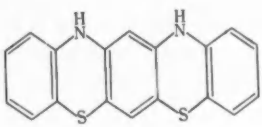
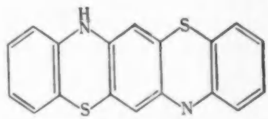
The preparation of II was attempted by fusing *NN'*-diphenyl-*p*-phenylenediamine with four equivalents of sulphur. The second ring closure could of course occur so as to give an angular isomer of II. However, after a long fractional sublimation *in vacuo*, only a small amount of a compound analysing correctly for II was obtained and no attempt to confirm that it had the linear structure was made. Chromatography of the more soluble fraction of the reaction mixture did not show any of the expected intermediate 3-anilidophenothiazine (V), even when only two equivalents of sulphur were used.



(I)



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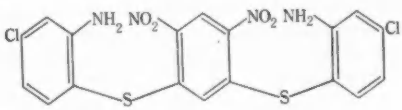
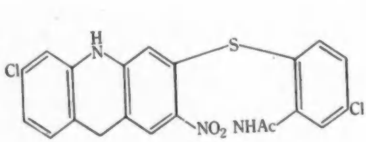
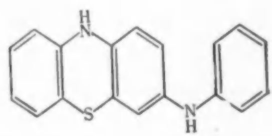


(III)



(IV)



(V)

It was thought that an alternate route to II or its isomer might lie in a sulphur fusion of V. However, 3-anilidophenothiazine could not be obtained by heating 3-aminophenothiazine (Bernthsen 1887) with bromobenzene in nitrobenzene or decalin in the presence of potassium bicarbonate and copper powder. A reaction carried out under similar conditions with 3-iodophenothiazine (Cymerman-Craig, Rogers, and Warwick 1955) and aniline gave only a very small quantity of an unrecognizable product.

Experimental

Melting points are corrected. Analyses are by Dr. K. W. Zimmermann, C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne.

(*a*) *4,6-Di-(2-acetamido-4-chlorobenzenethio)-1,3-dinitrobenzene* (*III*).—Acetylation of the corresponding diamine with acetic anhydride in acetic acid gave yellow *plates*, m.p. 121 °C (decomp.) from aqueous alcohol in 30% yield (Found: C, 46·9; H, 2·9; N, 9·6%. Calc. for $C_{22}H_{16}O_6N_4S_2Cl_2$: C, 46·5; H, 2·8; N, 9·9%). The corresponding dibenzoyl derivative was prepared in 60% yield by the action of benzoyl chloride on the amine in pyridine. It crystallized from acetone in clusters of yellow needles, m.p. 213 °C (Found: C, 55·5; H, 3·2; N, 8·3%. Calc. for $C_{32}H_{20}O_6N_4S_2Cl_2$: C, 55·6; H, 2·9; N, 8·1%).

(*b*) *2-(2-Acetamido-4-chlorobenzenethio)-3-nitro-8-chlorophenothiazine* (*IV*). — The preceding acetyl derivative (160 mg) in anhydrous acetone (2 ml) was treated on the water-bath with five successive equivalents of sodium hydroxide in ethanol at intervals of ½ hr. The solution was refluxed for another ½ hr and after removal of most of the acetone poured into water. Several recrystallizations from ethanol gave dark red *needles* (30 mg), m.p. 271 °C (decomp.) (Found: C, 49·9; H, 2·9; N, 8·8; Cl, 15·1%. Calc. for $C_{20}H_{13}O_3N_3S_2Cl_2$: C, 50·0; H, 2·7; N, 8·8; Cl, 14·9%), $\lambda_{max.}$ 260 mμ.

(*c*) *2-(2-Benzamido-4-chlorobenzenethio)-3-nitro-8-chlorophenothiazine.*—The benzoyl derivative described in (*a*) (320 mg), when treated as described in (*b*), gave dark red needles (50 mg) (from benzene and light petroleum), m.p. 238 °C (decomp.) (Found: N, 7·9%. Calc. for $C_{25}H_{15}O_3N_3S_2Cl_2$: N, 7·8%), $\lambda_{max.}$ 231 and 259 mμ.

(*d*) *4,6-Di-(2-aminobenzenethio)-1,3-dinitrobenzene.*—A solution of *o*-aminobenzenethiol (10·6 g) and sodium hydroxide (3·4 g) in dry ethanol (40 ml) was carefully added to a warm solution of 1,3-dichloro-4,6-dinitrobenzene (10·8 g) in ethanol (40 ml) and the mixture finally refluxed for 1 hr. After cooling, the dark yellow *plates*, m.p. 252 °C (decomp.), were collected (15·4 g) and washed with ethanol and water, unchanged by recrystallization from benzene (Found: C, 52·1; H, 3·4; N, 13·5%. Calc. for $C_{18}H_{14}O_4N_4S_2$: C, 52·2; H, 3·4; N, 13·5%). *Diacetyl* derivative, yellow needles (from acetone and ethanol), m.p. 213 °C (Found: C, 53·5; H, 3·9%. Calc. for $C_{22}H_{18}O_6N_4S_2$: C, 53·0; H, 3·6%). *Dibenzoyl derivative* yellow plates (from toluene), m.p. 225 °C (Found: C, 62·1; H, 3·8%. Calc. for $C_{32}H_{22}O_6N_4S_2$: C, 61·7; H, 3·5%). No absorption between 230 and 265 mμ.

(*e*) *2-(2-Benzamidobenzenethio)-3-nitrophenothiazine.*—Smiles rearrangement of the preceding benzoyl compound as in (*b*), followed by adsorption on magnesium oxide from benzene and elution with acetone gave orange *plates* (from benzene in 10% yield), m.p. 264 °C (decomp.) (Found: C, 64·3; H, 3·7; O, 10·5; S, 13·6%. Calc. for $C_{25}H_{17}O_3N_3S_2$: C, 63·6; H, 3·6; O, 10·2; S, 13·6%), $\lambda_{max.}$ 260 mμ.

(*f*) *2-(2-Acetamidobenzenethio)-3-nitrophenothiazine.*—Smiles rearrangement of the acetyl derivative described in (*d*) as in the preceding paragraph gave a small yield of dark red *plates* (from ethanol), m.p. 174 °C (decomp.) (Found: C, 59·3; H, 3·8%. Calc. for $C_{18}H_{13}O_2N_3S_2$: C, 59·0; H, 3·6%), $\lambda_{max.}$ 260 mμ.

(*g*) *5,12-Dithia-7,14-diazapentacene* (*II ?*).—*NN'*-Diphenyl-*p*-phenylenediamine (Calm 1883) (2·0 g) was heated at 170–190 °C with sulphur (0·99 g) and iodine (0·1 g) for 1 hr. The product was extracted with hot benzene, which dissolved only a small amount of material. The dry residue (2·4 g) was dark and of high m.p. Fractional sublimination of 0·4 g of the residue at 0·01 mm gave a light coloured fraction (27 mg) which sublimed between 230 and 280 °C, followed by a yellow-brown fraction between 310 and 330 °C. Resublimation of this fraction gave yellow plates (46 mg), m.p. 360 °C (Found: C, 66·8; H, 3·9%. Calc. for $C_{18}H_{12}N_2S_2$: C, 67·5; H, 3·8%).

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PREPARATION OF PHLOROGLUCINOL TRIMETHYL ETHER*

By J. W. Clark-Lewis†

Preparation of alkyl ethers from phloroglucinol and alkyl halides or sulphates is complicated by formation of *C*-alkyl derivatives due to keto-enol tautomerism of the phenol. However, a further consequence of this tautomerism is that dialkyl ethers can be obtained from phloroglucinol and alcohols under conditions resembling Fischer-Speier esterification of acids. The dimethyl ether, prepared in this way by Weidel and Pollak (1900) and by Pratt and Robinson (1924), can then be methylated without difficulty to phloroglucinol trimethyl ether (Freudenberg 1920); Touchstone, Ashmore, and Huffman (1956) recently described various other trialkyl ethers obtained from phloroglucinol by this two-stage method. Bredereck, Hennig, and Rau (1953) have reported the first satisfactory preparation of phloroglucinol trimethyl ether (93 per cent.) directly from phloroglucinol, with inhibition of *C*-alkylation by maintaining pH 8–9 throughout the methylation by gradually adding aqueous sodium hydroxide. An experimentally simpler and more convenient alternative is the methylation of anhydrous phloroglucinol by the standard anhydrous acetone–potassium carbonate technique as described below.

Experimental

Anhydrous potassium carbonate (130 g; 4 equiv) was added to a solution of anhydrous phloroglucinol (30 g) in dried (K_2CO_3) acetone (300 c.c.), and the mechanically stirred suspension was warmed almost to the reflux temperature before adding four quantities ($3\times22\cdot5$ and 1×10 c.c.) of freshly washed and dried ($MgSO_4$) dimethyl sulphate (total 77·5 c.c.; 3·5 equiv) at intervals of 15 min. Heating was discontinued after 3 hr (total), and the suspension was stirred for a further 1 hr after the addition of water (300 c.c.) and aqueous ammonia (*d* 0·88; 25 c.c.); water was then added to dissolve salts and the solution was extracted with ether. The ether extract was washed once with dilute hydrochloric acid, three times with aqueous sodium hydroxide, and finally with water before evaporation of the solvent. The residue was distilled at the water-pump and the pale yellow distillate solidified (34·1 g, 85%), m.p. 45–48·5 °C; recrystallization from methanol (30 c.c.) at 0 °C gave phloroglucinol trimethyl ether in colourless prisms (24·8 g, 62%), m.p. 52–53 °C (Found: C, 64·1; H, 7·1; OMe, 55·1%. Calc. for $C_9H_{12}O_3$: C, 64·3; H, 7·2; OMe, 55·4%), and a further quantity (2·2 g, total 27 g, 67·5%) was obtained from the mother liquors. In a similar experiment the anhydrous acetone solution of methylated product was filtered from inorganic salts, and the filtrate was concentrated by evaporation before being shaken with dilute aqueous sodium hydroxide and ammonia solution until the product (34 g, 85%) solidified (m.p. 42–46 °C); recrystallization from methanol (charcoal) gave colourless prisms of phloroglucinol trimethyl ether, m.p. 52–53 °C.

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CHANGE OF 2,4-DINITROPHENYLHYDRAZONES ON ALUMINA AND SILICA GEL CHROMATOGRAPHIC COLUMNS*

By D. A. FORSS† and E. A. DUNSTONE†

In an investigation of the " cardboard " flavour in skim milk (Forss, Pont, and Stark 1955*a*, 1955*b*), the compounds responsible for this defect were found to be the C_{5-11} 2-enals and the C_{6-11} 2,4-dienals. These unsaturated aldehydes were separated by passing their 2,4-dinitrophenylhydrazones through chromatographic columns. While these derivatives passed unchanged through alumina and silica gel columns when developed with ether and light petroleum, some of the 2,4-dinitrophenylhydrazones of the aliphatic saturated aldehydes and ketones which were also present were observed to change. Acetaldehyde 2,4-dinitrophenylhydrazone was the main product of these changes but formaldehyde and other 2,4-dinitrophenylhydrazones were also obtained. The proportion changed was greater when relatively small amounts of the 2,4-dinitrophenylhydrazone were applied to the column, and the effect was much more marked on silica gel than on alumina.

Since alumina and silica gel columns have been widely used for the fractionation of 2,4-dinitrophenylhydrazones (Gordon *et al.* 1951) and since further work on mixtures of aliphatic carbonyl compounds was contemplated in this laboratory, a study was made of the factors responsible for these changes.

Use of ethanol in place of ether, use of other brands of silica gel, washing the gel with hydrochloric acid to remove iron, and extensive washing with water to remove hydrochloric acid, all failed to suppress the changes.

It is possible that 2,4-dinitrophenylhydrazones and carbonyl compounds present in the solvents enter into an exchange reaction, but then the use of carbonyl-free solvents should suppress the changes, but this was not so.

There exists the possibility that carbonyl compounds are produced during the passage of the solvent through the column and, while the reason for this

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has so far eluded us, the conclusion nevertheless is that silica gel adsorption columns should not be used for the fractionation of mixtures of the 2,4-dinitrophenylhydrazones of saturated aliphatic aldehydes and ketones. There is much less risk in using alumina columns. Good separation without change can be obtained on cellulose partition columns with methanol and light petroleum (b.p. 100–120 °C) as solvents.

Experimental

Glass columns 30 by 1 cm were used for amounts of 2,4-dinitrophenylhydrazones up to 2 mg and columns 50 by 2 cm for amounts from 2 to 50 mg.

(*a*) *Identification of Compounds.*—All compounds obtained from chromatographic columns were characterized by measurement of their light absorption maxima in ethanol and their R_F values on paper with methanol and light petroleum (Meigh 1952). Because formaldehyde and acetaldehyde 2,4-dinitrophenylhydrazones occurred most frequently further support for their identity was sought. These derivatives sublime, which makes their melting point determination more difficult. When samples of authentic and of isolated formaldehyde 2,4-dinitrophenylhydrazone were placed between two microscope coverslips and placed on a Fisher type micromelting point apparatus at 150 °C, both samples sublimed rapidly and the freshly formed crystals melted at 162–163 °C and 162–164 °C respectively. The melting behaviour of acetaldehyde 2,4-dinitrophenylhydrazone is further complicated by the fact that it exists in a number of forms with different melting points. It melted at 147 °C, which indicated that it was a mixture of the " metastable " form which melts at 157 °C and the " stable " form which melts at 168 °C (Huntress and Mulliken 1946).

Infra-red spectra of " Nujol " mulls of the formaldehyde and acetaldehyde 2,4-dinitrophenylhydrazones were determined by Dr. J. B. Willis, Division of Industrial Chemistry, C.S.I.R.O. The spectra of the isolated and authentic samples of the formaldehyde derivative were identical. The infra-red spectrum of the isolated acetaldehyde 2,4-dinitrophenylhydrazone differed from the authentic sample submitted but reference to the work of Ross (1953) showed that the isolated compound contained about 95% of the lower melting crystalline form and about 5% of the higher melting crystalline form of acetaldehyde 2,4-dinitrophenylhydrazone, while the authentic sample submitted was the higher melting form.

(*b*) *Alumina Columns.*—Acetone 2,4-dinitrophenylhydrazone was the only compound observed to change on an alumina column. When it was developed with 2% ether in light petroleum, about 75% of the acetaldehyde 2,4-dinitrophenylhydrazone and about 25% of a 2,4-dinitrophenylhydrazone with R_F value and light absorption maximum of butanone-2, were obtained. The 2,4-dinitrophenylhydrazones of *n*-pentanal, *n*-hexanal, and octanone-2 passed unchanged through an alumina column.

(*c*) *Silica Gel Columns.*—Change on a silica gel column was first noticed when *n*-hexanal 2,4-dinitrophenylhydrazone, isolated from an alumina column, was rechromatographed on a silica gel column with ether and light petroleum. There was complete conversion to the acetaldehyde derivative. When the synthetically prepared *n*-hexanal derivative was developed on a similar column, the same effect was noted. With ethanol in place of ether similar results were obtained.

Acetone 2,4-dinitrophenylhydrazone, when developed on silica gel with ether and light petroleum, was mainly converted to the acetaldehyde derivative, but the formaldehyde 2,4-dinitrophenylhydrazone and a 2,4-dinitrophenylhydrazone with R_F value and light absorption maximum of *n*-hexanal were also obtained. When ethanol and light petroleum were used as developers, the effect was similar. The addition of one part of celite (Johns Manville " Celite 545 ") to two parts of silica gel did not prevent the change nor did the use of columns packed with Mallinckrodt A.R. " Silicic Acid " or Davison " Selective Adsorption Silica Gel 950 ".

Propionaldehyde 2,4-dinitrophenylhydrazone on silica gel with ether and light petroleum as solvent partly changed to the acetaldehyde derivative.

The changes on silica gel columns became appreciable only after 24 hr. When a mixture of the 2,4-dinitrophenylhydrazones of acetone, butanone-2, hexanone-2, and undecanone-2 was developed on a silica gel column with ether and light petroleum for 2 days, the bulk of the 2,4-dinitrophenylhydrazones of hexanone-2 and undecanone-2 passed through unchanged, but the slower moving hydrazones of acetone and butanone-2 could not be recovered.

Up to this stage, the solvents, which were of analytical reagent quality, had not been treated to remove traces of carbonyl compounds. Treatment to remove carbonyl compounds did not affect the exchange. Preliminary passage of carbonyl-free solvent through a column containing 2,4-dinitrophenylhydrazine, before adding acetone 2,4-dinitrophenylhydrazone and passing it through a second column, brought about no improvement. Avoiding exposure of the column to light had no effect. When the silica gel, from a column in which acetone 2,4-dinitrophenylhydrazone had been developed with partial breakdown, was thoroughly washed with ether and light petroleum, dried for 12 hr at 110 °C, and repacked into a column, acetone 2,4-dinitrophenylhydrazone again broke down.

The possibility that traces of HCl in the silica gel might be catalysing the change was eliminated when it was found that after prolonged washing of the silica gel with water, the characteristic rearrangement still occurred. The silica gel was prepared by the method of Fairbairn and Harpur (1951), and contained iron. When the silica gel was repeatedly washed with $1 \times N$ HCl to remove the iron, alteration of acetone and *n*-hexanal 2,4-dinitrophenylhydrazones still took place.

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THE VOLATILE LEAF OIL OF *MELALEUCA ERICIFOLIA* SM.*

By R. O. Hellyer†

The first chemical examination of the oil of *Melaleuca ericifolia* Sm. was made by Baker and Smith (1922), who reported α-terpineol to be the characteristic constituent, finding also cineole, (+)-α-pinene, (+)-limonene, dipentene, and sesquiterpenes to be present. However, Penfold and Morrison (1935), in a re-examination of the oil from various localities of New South Wales (including that from which Baker and Smith obtained their material), could find no α-terpineol, but showed that (+)-linalool was the characteristic component.

The commercial distillation of this species has recently been projected and a more critical examination of the oil has become desirable in order to resolve the earlier conflicting data. The examination of oils distilled by a commercial firm on the North Coast of New South Wales and those distilled by the author from localities near Sydney has confirmed the presence of linalool to the extent of about 20 to 40 per cent. However, in the oil distilled from a " bulk cut " of foliage from Narrabeen, N.S.W., the presence of about 4 to 5 per cent. of (+)-α-terpineol was demonstrated. Other constituents found were: cineole (21 per cent.), linalool (approx. 25 per cent.), terpenes (approx. 15 per cent., consisting of (+)-α-pinene, dipentene), sesquiterpenes, two sesquiterpene alcohols both yielding an azulenic compound on dehydrogenation, and an alkane. Traces of aldehydes were present in the lowest-boiling fraction.

To determine whether there are any plants which yield oils with α-terpineol as the characteristic constituent, the physical constants of the oils distilled from nine individual plants were compared. No significant variations were observed, each oil containing linalool and cineole.

Since the physicochemical properties of their oil were similar to those of oils containing linalool, it would appear that Baker and Smith overlooked the presence of linalool in the oil they examined. There is no possibility that they worked on the wrong species, as the only plant which is likely to be confused with *M. ericifolia* Sm. is *M. erubescens* Otto. However, *M. erubescens* is always red-flowered (Cheel 1924) and Baker and Smith definitely state that they worked on white-flowered material, that is, *M. ericifolia*.

Experimental

Microanalyses were carried out by Dr. K. W. Zimmermann at the C.S.I.R.O. Microanalytical Laboratory at the University of Melbourne.

The crude oils were obtained by the steam-distillation of the leaves and terminal branches, cut as for commercial distillation. The bulk cuts of leaves were distilled in a tin-lined apparatus,

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TABLE 1

PHYSICOCHEMICAL DATA ON CRUDE OILS OF M. ERICIFOLIA

Locality	Date Received	Wt. of Foliage (lb)	Oil Yield (%)	d_{15}^{15}	n_D^{20}	$[\alpha]_D$	Solubility (in 70% w/w aqueous alcohol)	Acid Number (mg KOH/g)	Ester Number		Cineole Content* (%)	Linalool Content† (%)
									mg KOH/g	After Acetylation		
Jones I., Taree, N.S.W.	6.x.54	—	—	0·8984	1·4755	+13·20°	Soluble in 1·5 vol	1·3	6	142	11·9	36
				0·9058	1·4783	+13·20°	Soluble in 1·35 vol	1·9	8	140	—	—
				0·9102	1·4801	+10·25°	Insoluble in 10 vol	1·8	6·5	119	—	—
Narrabeen, N.S.W.	2.viii.55	162	0·60	0·9054	1·4746	+10·40°	Soluble in 1·5 vol	1·0	6·4	95	20·7	25

* All cineole determinations (Cocking method) done on fractions boiling up to 70 °C at 10 mm pressure.

† Linalool contents calculated from fractional-distillation data.

and the single plants in glass cohobation stills described by McKern and Smith-White (1948). The physical constants of the oils were determined after drying with anhydrous sodium sulphate. All melting points are uncorrected.

The analytical data for the bulk cuts from Narrabeen and Taree are given in Table 1.

TABLE 2

FRACTIONAL DISTILLATION OF CRUDE OIL

Fraction	Boiling Range (°C at 10 mm pressure)	Volume (ml)	d_{15}^{15}	$[\alpha]_D$	n_D^{20}
1	41– 66	150	—	—	
2	66– 79	14	0·8890	+ 6·40°	1·4663
3	79– 82	90	0·8748	+15·20°	1·4641
4	82– 95	10	0·8884	+13·20°	1·4688
5	95–100	10	0·9286	+10·40°	1·4826
6	100–110	8	0·9296	+ 8·00°	1·4873
7	110–119	10	0·9266	+ 6·00°	1·4945
8	119–121	21	0·9268	+ 9·20°	1·5000
9	121–140	33	0·9396	+11·60°	1·5038
10	140–144	20	0·9811	+ 4·00°	1·5051
Residue	>144	10		Solidified	
Trap	—	5	—	+18·00°	1·4602

Crude oil (400 ml) from bulk cut (Narrabeen ; August 2, 1955) was fractionally distilled at reduced pressure through a Widmer type column. The resulting fractions are presented in Table 2.

(*a*) *Aldehydes*.—The contents of the dry ice-acetone trap gave a slight colour with Schiff's reagent, but no 2,4-dinitrophenylhydrazone could be prepared.

TABLE 3

FRACTIONAL DISTILLATION OF CINEOLE-FREE TERPENES

Fraction	Boiling Range (°C at 20 mm pressure)	Volume (ml)	d_{15}^{15}	$[\alpha]_D$	n_D^{20}
1_T	54–56	11	0·8634	+34·00°	1·4665
2_T	56–68	14	0·8648	+24·00°	1·4688
3_T	68–74	17	0·8673	+ 4·00°	1·4748
4_T	74–78	6	0·8648	+ 3·00°	1·4778

(*b*) *Cineole*.—Fraction 1 was washed twice with 50% aqueous resorcinol solution. On steam-distillation of the basified cineole-resorcinol addition compound solution, a colourless oil of camphor-like odour was obtained having d_{15}^{15} 0·9237 ; $[\alpha]_D$ ±0° ; n_D^{20} 1·4590. The identity of the cineole was confirmed by the preparation of the o-*cresol addition compound*, m.p. 57 °C, undepressed by an authentic specimen. The cineole-free oil from fraction 1 was refractionated at reduced pressure to give the fractions described in Table 3.

(*c*) (+)-α-*Pinene*.—Fraction 1_T gave a *nitrosochloride*, m.p. 111·5 °C, undepressed by an authentic specimen of α-pinene nitrosochloride.

(*d*) *Dipentene and* (+)-*Limonene*.—Fraction 3_T in glacial acetic acid readily yielded a *bromide*, m.p. 124–125 °C, undepressed by an authentic specimen of dipentene tetrabromide. The slight dextro-rotation of fraction 3_T suggests the presence of (+)-limonene, but the tetrabromide could not be obtained.

(*e*) (+)-*Linalool*.—Fraction 3 gave a *phenylurethane*, m.p. 64·5–65·5 °C, undepressed by an authentic specimen of the phenylurethane of linalool.

(*f*) (+)-α-*Terpineol*.—Fraction 5 gave a *phenylurethane*, m.p. 109·5–110 °C, undepressed by an authentic specimen of the phenylurethane of α-terpineol. Fraction 6 gave the same derivative.

(*g*) *Sesquiterpenes*.—Fraction 8 (10 ml) was examined for aromadendrene by shaking at 0–5 °C with potassium permanganate solution (8%). A mixture of liquid acids was recovered, but no aromadendrone could be detected. Fraction 9 was eluted from an alumina column with light petroleum (b.p. 60–80 °C) to separate any oxygenated constituents. The recovered oil was then distilled over sodium at a reduced pressure, and an oil having the following constants was obtained: b_{10} 124–129 °C; d_{15}^{15} 0·9290; n_D^{20} 1·5036; $[\alpha]_D$+15·0°. This sesquiterpene, which on sulphur dehydrogenation gave a blue *azulene*, did not give a solid hydrochloride, but gave an unstable *nitrosochloride*, m.p. 105·5 °C (decomp.) (Found: C, 65·7; H, 8·7; N, 4·4; Cl, 14·5%).

(*h*) *Sesquiterpene Alcohols*.—By chromatography on alumina, fraction 10 was separated into two alcohols, one being a very viscous oil of d_{15}^{15} 0·9893; n_D^{20} 1·5035; $[\alpha]_D$ −11·50° (Found: C, 80·5; H, 11·9; O, 8·4%, the other, a mobile oil of d_{15}^{15} 0·9888; n_D^{20} 1·5061; $[\alpha]_D$ +4·00° (Found: C, 81·5; H, 11·4; O, 7·2%. Calc. for $C_{15}H_{26}O$: C, 81·0; H, 11·8; O, 7·2%). Both oils on dehydrogenation with sulphur gave a blue *azulene*.

(*i*) *Alkane*.—The still-pot residue solidified on standing, and after removing excess oil on a porous plate, a *solid alkane*, m.p. 52–53 °C, was obtained after purification by elution from an alumina column with light petroleum (b.p. 60–80 °C).

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